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THE JOURNAL

—OF THE—

AMERICAN CHEMICAL SOCIETY.

VOLUME XXV.

1903.

PART II

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THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN
UNIVERSITY, MIDDLETOWN, CONN.]

DESCRIPTION OF A BOMB-CALORIMETER AND METHOD OF ITS USE.

BY W. O. ATWATER AND J. F. SNELL.

Received May 26, 1903.

THE apparatus of which an account is here given was first described in 1895.¹ The present description is, in part, a revision of one published in 1897.² Experience since the latter article was written has led to further improvements in the bomb and accessory apparatus. A number of the improvements have been devised by Mr. Blakeslee, formerly mechanician of Wesleyan University; others were suggested by Dr. F. G. Benedict, who has had much to do with its use, and by Messrs. Dinsmore and Singleton, of Middletown, Conn., by whom the apparatus is now made.

The bomb is a modification of that of Berthelot.³ The latter is most excellent; the only objection to it is its great cost, which is due to the large amount of platinum in the cover and lining.

¹ "A New Form of Bomb-Calorimeter," by W. O. Atwater and Chas. D. Woods. Report of the Storrs (Conn.) Experiment Station for 1894, p. 135.

² "Improved Forms of Bomb-Calorimeter and Accessory Apparatus," by W. O. Atwater and O. S. Blakeslee. Report of the Storrs (Conn.) Experiment Station for 1897, p. 199.

³ "Sur la force des matières explosives," I, 225 and *Ann. chim. phys.*, (5) 6, 546.

Various modifications of the Berthelot apparatus have been devised to obviate the expense of the platinum. Mahler uses a bomb of forged steel, with enamel lining. Hempel uses, for the determination of heats of combustion of coal, a simple bomb of steel without lining. In accordance with suggestions by one of us (W. O. A.) during a sojourn in Dresden, Professor Hempel most kindly had a bomb made by the mechanics who make the bombs of his devising, and lined by Heraeus of Hanau with a thin sheet of platinum. Thanks to Professor Hempel's painstaking care, added to his inventive skill and his familiarity with the subject, the bomb proved very efficient. With modifications from time to time, it has gradually assumed its present form. The principle is the same as in Berthelot's bomb, but whereas the cover of Berthelot's fits into the cylindrical cup like a very wide stopper, the cover in this, as in Mahler's, rests directly on the upper edge of the cup.

The purpose of the present article is to describe the bomb and accessory apparatus and the method of their use in the determination of the heats of oxidation of foods, feeding-stuffs and products of animal metabolism, a kind of work for which the apparatus has been in almost constant use in this laboratory for some ten years. Experience here and elsewhere shows that the apparatus may be advantageously employed for determining sulphur and phosphorus in organic compounds, as well as for determining the heats of combustion of coal and other fuel materials, but the special ways by which it is best employed for these purposes will be more fitly described at another time.

The method of determining heats of combustion is essentially the procedure of Berthelot as modified by Stohmann.¹ It has been gradually developed in this laboratory under the hands of Messrs. C. D. Woods, F. G. Benedict, O. F. Tower and the authors.

I. DESCRIPTION OF THE APPARATUS.

The method consists essentially in burning the substance in excess of oxygen at high pressure in a bomb immersed in water, the heat of combustion being determined by the rise in the temperature of the water. The apparatus consists of:

(1) The calorimeter proper, including the bomb, a britannia-metal cylinder to hold the water in which the bomb is immersed, a thermometer and a stirrer. The term *calorimeter system* is here

¹ *J. prakt. Chem.*, 147, 503 (1889). See also Berthelot: "Traité pratique de calorimétrie chimique," p. 128.

used to denote the bomb and contents, the metal cylinder and the immersed parts of the thermometer and stirrer, together with the water.

(2) Two concentric protecting-cylinders of "indurated fiber" with cover. These enclose the calorimeter system and insulate it so as to prevent rapid passage of heat between it and the outside air.

(3) Accessory apparatus, including a clamp and spanner for closing the bomb, appliances for filling the bomb with oxygen (bomb-support, coupling and manometer), a mould and press for moulding powdered substances, which are to be burned, into pellets, electrical appliances for igniting the charge, and machinery for operating the stirrer.

The Bomb.

The bomb consists of three parts: A cylindrical *cup* to contain



Fig. 1.—Parts of the bomb. Cup, cover with capsule holder, capsule and collar.

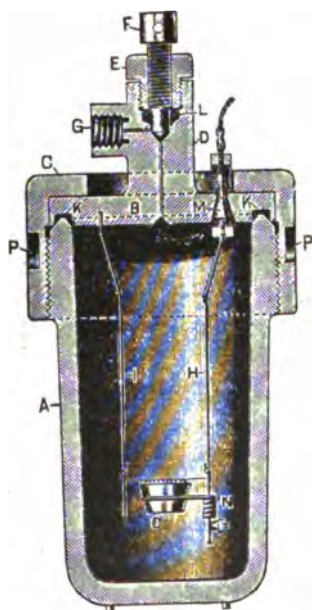


Fig. 2.—Cross-section of the bomb.

the substance to be burned and the oxygen for combustion, a *cover* to close the cup, and a threaded ring or *collar* to hold the cover tightly on the cylinder. With these is a metal capsule to hold the substance. The parts are shown separately in Fig 1, and in cross-section, as put together, in Fig. 2.

The cup is of Hotchkiss gun tool steel, kindly furnished by the Bethlehem Iron Company, which has favored us with tests of "oil-tempered forgings made from the same steel, and at about the same time the bars were made" which were used for the later bombs. These latter tests "were many in number, and an average taken from them gives the following results":

Tensile strength.....	85,514 lbs. per sq. in.
Elastic limit	47,366 " " "
Extension	23.82 per cent.
Contraction	43.05 per cent.

The cover (B), collar (C), and screws (E, F) are of the best tool steel.

In the apparatus as now made the inside dimensions of the cup are, approximately: Depth, 12.7 cm.; diameter, 6.3 cm. at top and 5.9 cm. at bottom. The wall is approximately 0.6 cm. in thickness. The weight of the whole bomb is not far from 3,200 grams, and its capacity nearly 380 cc.

The cover is lined on the bottom with platinum and is provided with a neck (D). Into this fits, at the top, a cylindrical screw (E), into which in turn fits a valve screw (F). In the neck (D), where the bottom of the cylindrical screw (E) rests, is a shoulder fitted with a packing of lead (L). The pressure of the valve screw on this packing makes a tight closure upon the part of F which it surrounds. On the side of D is an opening (G), into which may be screwed the coupling connecting the tube with the receptacle which holds the oxygen used for the combustion (see Fig. 8). The coupling, when screwed in, thrusts against a washer of lead at the end of G, which insures perfect closure. A narrow passage runs horizontally to a point just above the valve seat in the center of D. A similar passage runs from the apex of the valve seat perpendicularly downwards through the cover. These two passages provide a channel for the oxygen to pass into the interior of the bomb. This channel may be tightly closed by the valve screw, the lower end of which is conical and thrusts against the inner surface of D, the angle of which at the place of contact corresponds to that of the tip of the screw. Between the top of the valve seat and the bottom of the packing (L), the valve screw fits so closely in the cover as to prevent the lead of the packing from working downward and thus obstructing the small gas passages. After continued use, the valve of the bomb may be

found to leak a little on account of corrosion of the conical end of the valve screw by nitric acid and moist oxygen. It should then be reseated by an expert mechanic. The lead washer (G) and valve packing (L) will require to be replaced after long use.

The upper edge of the cup (A) is beveled on both sides; the apex is rounded and fits into a gasket (K) of lead, which is held in a recess or groove in the cover (B). With use, the metal gradually flows out of the groove under the heavy pressure so that the gaskets have to be replaced occasionally. The gasket may be removed from the groove in the cover by cutting it nearly in two with the tool provided for the purpose and prying it up in such way as to sever it. In using the tool, great care must be taken not to injure either the platinum lining of the cover or the sides and bottom of the groove. Attempts have been made to substitute harder metals for lead in the gaskets, but lead has been found most satisfactory as least liable to injure the platinum lining against which it presses. Extra gaskets are furnished with the bomb. In closing the bomb, it is important that the friction between the cover and collar should be reduced as much as possible. The surfaces of contact of the two pieces should, therefore, be well oiled.

The platinum wires (H) and (I), inside the bomb, serve to hold the capsule (O) containing the substance to be burned and to conduct an electric current for igniting it. Of these two wires, one (I) is screwed into the cover; the other (H) passes through a conical hole in the cover and is insulated from the metal. The method of insulating the wire is shown in Fig. 3. In the bomb

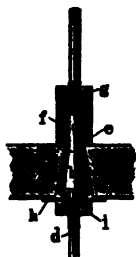


Fig. 3.—Method of insulation.

cover, a section of which is shown at a, is a conical hole. The larger end of the hole is on the inside of the cover. Into the hole fits the conical enlargement (b) of the German silver rod (c) which projects above the cover and serves for the electrical connection. The platinum wire (d) is gold-soldered into the lower

end of the cone, thus making a continuous conductor (c, b, d). To insulate this conductor, a piece of rubber tubing of $\frac{3}{32}$ inch (2.5 mm.) inside diameter is pushed down over the cone until it projects 1 to 2 mm. beyond the base. The free end of the tubing is threaded through the hole in the bomb cover and drawn up until the cone is in place; the surplus rubber tubing is then cut off at e, and over the rod (c) is placed the hard rubber sleeve (f) and the nut (g) is tightened down until the conductor (c, b, d) is firm in the cover. A mica disk (h) is placed over the platinum wire (d), and held against the lining of the cover by the platinum nut (i). This disk serves both to protect the insulating rubber from combustion and to prevent the nitric acid formed in the bomb from penetrating into the conical hole in the cover and causing leakage of current and corrosion of the German silver and steel. If a little space at the large end of the cone is left unfilled by the end of the rubber tubing, it is filled with a mixture of fine asbestos fiber and shellac, which is allowed to dry before the mica disk (h) is secured in place. Whenever the insulation of the wire becomes poor, the rubber covering of the conductor should be replaced by a new one.

Near the lower end of H (Fig. 2) is a platinum wire bent in the form of a ring to hold the capsule, and coiled about the wire, to which it is held by a platinum thumb-nut. When a combustion is made, the two platinum wires are connected by a very fine iron wire which passes over the capsule and is heated by the electric current. The part directly above the substance to be burned is wound into a spiral, thus furnishing a larger quantity of iron to be ignited and, falling, to ignite the substance in the capsule.

Linings of Cup and Cover.—Both cup and cover are lined with platinum or gold-plated copper. The lining of the *cover* is sweated onto the steel. A platinum plug fitted into the vertical passage by which the gas enters serves to protect the steel surfaces of the valve seat and oxygen-channel from corrosion by the dilute nitric acid which condenses on the lining of the cover and which might otherwise be carried out into the channel when the valve is opened. The oxygen is admitted through the plug by a tubular passage, the outlet of which is horizontal, so that the current of gas may not blow directly upon the substance in the capsule.

The lining of the *cup* is made from a single sheet of metal which is spun to fit the steel cup accurately. It can be easily removed

from the latter by placing the fingers of the left hand inside the lining, and the thumb against the threads of the cup (which may be wrapped with cotton to protect the thumb), and drawing outward upon the lining, at the same time tapping the steel cup with a wooden mallet. The lining should be removed occasionally and any rust that may have formed on the inner surface of the steel polished off. Before the lining is put in again, the steel cup should be wiped out with a cloth moistened with oil.

For the lining, platinum has been used and has proved entirely satisfactory not only here but in other laboratories, but its high cost is an objection, and numerous attempts have been made to find a cheaper substitute. The Mahler bomb, which is in use in many laboratories, has a lining of enamel. So far as we are informed, it is found satisfactory save that it is apt to crack and scale off. We have found that aluminum linings, spun from the purest metal we can obtain, are attacked by the nitric acid to such an extent as to interfere with the accuracy of the determinations. Attempts to electroplate the inside surface of a steel cup with platinum or gold have been made by Berthelot¹ and also by Professor H. W. Wiley, chief of the Bureau of Chemistry, U. S. Department of Agriculture, but the results have been unsatisfactory, the lining either having proved porous and thus permeable to the oxygen and nitric acid, or having blistered, probably on account of the unequal expansion of the steel and the plating.

The most satisfactory substitute we have found for the platinum lining is one of copper heavily electroplated with gold. A cup was spun for us by the Middletown (Conn.) Silver Company from No. 20 Brown & Sharp gauge (0.8 mm.) sheet copper and electroplated by the International Silver Company of Meriden, Conn. A light plating of silver, two of gold of about 1 dwt. (1.5 grams) each, and finally three of gold of about 2 dwts. (3 grams) each were applied, each plating being thoroughly burnished before the next was deposited. This lining was used for four months or more. It was only after some 300 combustions had been made in it that blisters formed in the gold plating in two places on the bottom of the cup, and not until after the 400th determination; that copper could be detected in the bomb rinsings (which always contain free nitric acid). The same lining was then replated with gold and was in good condition after use in over 500 additional

¹ *Ann. chim. Phys.*, (5), 23, 161.

determinations, when it was destroyed by an accident. Other linings of this description are now in use in different laboratories and while, at present, any positive conclusion as to their durability would be premature, it seems probable that, at least with occasional replating, a copper lining might serve for several thousand determinations.

In devising this gold-plated copper lining we have profited, particularly as regards the necessity of burnishing repeatedly during the deposition of the gold, by the experience of Mr. Henry J. Williams, of Boston, who has constructed and patented a calorimeter having a spherical bomb of aluminum bronze, electroplated internally with gold and externally with nickel. Mr. Williams' apparatus appears to have many excellent features. Its cost is, however, much beyond that of even the platinum-lined apparatus here described.

We have planned to use gold-covered copper ("rolled plate") instead of platinum for the lining of the cover but have as yet no experience in its use.

We find it a very decided advantage to have the lining and especially that of the cup easily removable. The low cost of gold-plated copper makes it easy to have two linings, so that if one gives out, it can be easily removed and repaired while the other is used in its place.

Metal Capsules.—The sample for combustion is held in a frustum-shaped metal capsule which is supported in the bomb as shown in Fig. 2. We employ capsules of three sizes: the small size, which is 1 cm. deep, 1.4 cm. in diameter at the base, and 1.6 cm. in diameter at the top, is used in most cases; the medium size, 1.7 cm. deep, 1.5 cm. in diameter at the base, and 2.2 cm. in diameter at the top, is employed for the combustion of urine absorbed in cellulose absorption blocks; the large size, 2 cm. deep, 1.5 cm. in diameter at the base, and 2.5 cm. in diameter at the top, is used in the combustion of milk upon asbestos (see below).

Until recently we have used exclusively capsules of platinum of the two smaller sizes. Those of the smallest size with a thickness of 0.15 mm. weigh only about 2 grams. They serve the purpose but are too thin for durability. A thickness of 0.20 to 0.25 mm. would be preferable. Those of the larger, *i. e.*, medium size, with a thickness of 0.35 mm. and weighing 7 grams, we find very satisfactory for use with the cellulose blocks employed for determining

the heat of combustion of urine. As the platinum capsules are rather expensive, we have recently used capsules of nickel. They are spun from $\frac{1}{64}$ inch (0.4 mm.) sheet nickel by the Goodwin & Kintz Company of Winsted, Conn., cost but a few cents each, and have thus far proved very satisfactory. To prevent their cracking, they are annealed and hammered and are so shaped that the sides join the base with a curve instead of a sharp angle. Before using, they are heated in the Bunsen flame until the surface is oxidized. When so treated, they withstand further oxidation for a considerable time even at the high temperature attained in the bomb.

Iron Wire.—The ignition of the sample in the bomb is brought about by means of a small coil of iron wire heated to ignition by an electric current. A spool containing about 25 grams of 0.007-inch (0.18 mm.) wire is furnished with each apparatus. This quantity, if cut into lengths of 2.5 inches (6.3 cm.) will suffice for about 2000 combustions. By use of a simple "wire-measure," devised by Mr. Osterberg of this laboratory, a large number of wires of equal length may be prepared at one time. This measure consists of a cylindrical piece of hard wood, 2 cm. or more in diameter, having a longitudinal groove 0.6 cm. wide and 1 to 1.5 cm. deep. The cylinder may be conveniently prolonged into a handle. The wire is wound about this measure in as many turns as desired. By inserting one blade of a pair of shears into the groove, all the turns are easily cut at once. The pieces of wire, so cut, are made into coils by winding upon a pin or needle, leaving a half-inch of straight wire on each end. If the aggregate weight of the first ten pieces cut at one time is the same as that of the last ten of the same lot, the average weight of the twenty may be assumed to represent the weight of each piece of the lot.

Thermometer.—The thermometer used in determinations of heats of combustion must be capable of measuring small differences of temperature with as high a degree of accuracy as possible, since the chief source of error in the determination lies in these measurements, as explained below. At the same time, if the calorimeter is to be used in an ordinary laboratory room, the thermometer must be one that can be used over a considerable range of actual temperature. In specific terms, it must be capable of making measurements of temperature differences of 2° to 3.5° , accurate to a few thousandths of a degree, at an initial temperature

of 12° and also at an initial temperature of 25° or even higher (the initial temperature of the calorimeter being 2° or 3° below the room temperature). The requisite accuracy and adaptability are combined in "metastatic" thermometers of the Beckmann type. We have used for the most part a thermometer of this type made by Fuess of Berlin-Steglitz. It has a large bulb about 5 cm. in length and 1 cm. in diameter and contains about 32 grams of mercury. The scale is 23 cm. in length, divided into 6° , graduated to hundredths and capable of being read to thousandths with the aid of a lens. We have also used the Beckmann thermometer manufactured by Goetze of Leipzig.

With thermometers of this type, in addition to the ordinary correction for variations in the bore of the capillary, a second correction is evidently necessary for the reduction of the degrees of the scale to true centigrade degrees, for it is obvious that when the thermometer is set for use at a low temperature, the quantity of mercury in the bulb will be greater and the expansion per true degree, therefore, greater than when it is set for a higher temperature. Our Fuess thermometers have been calibrated by the Physikalisch-technische Reichsanstalt. By interpolating between the data of the certificate furnished by the Reichsanstalt we construct tables giving the caliber correction for each 0.1° and the "correction for setting" for each degree. For use in the laboratory, these tables can be most conveniently mounted on cards. Since the correction for setting is most conveniently used in a form different from that given in the certificate, we think it worth while to illustrate how the one is derived from the other.

The certificate accompanying one of our thermometers states that when the thermometer is set at 0° and heated to 6° (with the mean temperature of the projecting thread of mercury at 15°), 1° of the scale is found equivalent to 0.991° C.; when the thermometer is set at 25° and heated to 31° (projecting thread, 22°), 1° of the scale is equivalent to 1.002° C.; and when the thermometer is set at 50° and heated to 56° (projecting thread, 26°), 1° of the scale is equivalent to 1.013° C. The correction for 1° rise on the arbitrary scale is, therefore, -0.009° when the zero of the thermometer corresponds to 0° C. and $+0.002^{\circ}$ when it corresponds to 25° C., and since the change of the correction between 0° and 25° is the same as between 25° and 50° , *viz.*, $+0.011^{\circ}$, we are justified in assuming that the change for each degree amounts

to $0.011^{\circ} \div 25 = 0.00044^{\circ}$. For any setting of the thermometer between 0° and 50° , therefore, the correction to be applied for each degree of observed rise of temperature is $-0.009^{\circ} + 0.00044n^{\circ}$ where n = the true temperature to which the zero of the thermometer corresponds. The values of this correction for each degree are calculated to the nearest ten-thousandth of a degree and entered in the table of corrections. We determine the corrections for the Goetze thermometer by comparison with a Fuess which has been calibrated as above described.

For the reason that there is some danger of breaking thermometers of this type by improper handling, particularly in the case of the Fuess thermometer with its very heavy bulb, we give, for the benefit of the inexperienced, the following directions for changing the setting :

To set a thermometer of the Beckmann type for use at a temperature higher than that at which it has last been used, the bulb is warmed in the hand or in water until the mercury fills the whole of the capillary tube and a part of the upper reservoir. A portion of the mercury is then shaken off into the upper reservoir. This separation of the mercury may be effected by holding the thermometer vertically in one hand and either (1) tapping the outer tube ("envelope") near the reservoir smartly but not violently with the fingers of the other hand; or (2) striking the hand which holds the thermometer vertically against the other hand. Of the two methods, the former will usually separate a smaller portion of mercury than the latter. The thermometer should never be held in a horizontal or oblique position when jarred in either of these ways, as the inertia of so large a mass of mercury may produce so severe a transverse strain in the glass envelope as to break it.

To set the thermometer at a lower temperature, the mercury contained in the upper reservoir is brought into the upper part of the reservoir by inverting the thermometer and tapping the brass knob at the top gently on the table. The mercury will remain in the upper part of the reservoir when the thermometer is reinverted, i. e., brought into normal vertical position with the bulb downward. The bulb is then warmed until the mercury in the capillary tube has joined that in the upper reservoir, then cooled until more or less of the mercury originally in the reservoir has been drawn into the capillary tube. The mercury remaining in the top of the reservoir is now separated and brought to the bottom by one of

the methods described above. With practice, the shifting of the mercury from capillary tube to reservoir, or *vice versa*, is easily and quickly accomplished.

Lens and Tapper for Thermometer.—The use of a lens to mag-

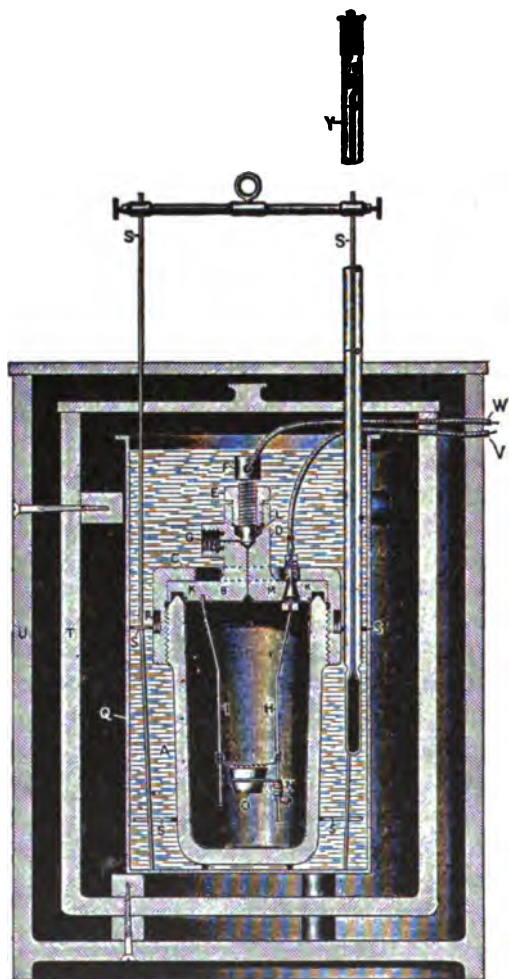


Fig. 4.—Bomb-calorimeter; apparatus as used for actual determinations of heats of combustion.

nify the divisions of the thermometer scale is essential. A Coddington lens of 1 inch (25 mm.) focal length (magnification = 10), made and mounted by the Bausch & Lomb Optical Co., Rochester, N. Y., has proved very satisfactory for this purpose.

For the prevention of errors of parallax, it is provided with an eye-hole and with a grooved adapter which fits against the envelope of the thermometer and serves to keep the principal axis of the lens at right angles to the thermometer scale.

To prevent lagging of the mercury in the capillary, the thermometer should be tapped on the brass cap, rather than on the glass envelope. A most useful and convenient tapper for this purpose is the hammer of a small electric bell which can be operated by a battery of two dry cells.¹ By means of a conveniently placed switch, the observer sets the hammer in motion a few seconds before each reading and stops it again after the reading is taken.



Fig. 5.—Bomb-calorimeter ready for a combustion.

Apparatus Mounted for Use.—The bomb, when ready for a combustion, is immersed in water contained in a metal cylinder. This cylinder is surrounded by concentric cylinders or pails of "indurated fiber," leaving air spaces to prevent undue passage of heat between the water and the outer air. The arrangement is shown in cross-section in Fig. 4 and, as it appears during a combustion, in Fig. 5.

¹ Such a tapper for a Beckmann thermometer was employed by Loomis (*Physical Review*, 1, 206 (1894)) and also by Orndorff and Cameron (*Am. Chem. J.*, 17, 517 (1895)).

Calorimeter Cylinder and Stirrer.—The cylinder is of britannia-metal 13 cm. in diameter, 23 cm. high, and holds, with the bomb, not far from 2 liters of water. A stirrer (SS), moved by a small motor or other agency, keeps the water in motion and insures the mixing needed for equalizing its temperature. This stirrer consists of two perforated annular pieces of sheet-brass connected by two brass rods which project out of the calorimeter and are there attached by thumb-screws to a nickel-plated cross-piece. A groove is cut in one side of the annular brass pieces to admit the thermometer. The calorimeter cylinder stands on cork supports which prevent it from coming in contact with the bottom of the pail. The interior of the britannia-metal cylinder should be kept clean and free from sediment.

The Outer Cylinders.—The diameters of the indurated fiber pails (U and T, Fig. 4) are such as to leave an air space of about 1 cm. between the two pails and one of 3 cm. between the inner pail and the calorimeter cylinder. The covers of the pails are of hard rubber. They are provided with holes for the two rods of the stirrer and for the thermometer. An adjustable standard attached to the outer pail (Fig. 5) bears an arm provided with a clamp for the support of the thermometer (Y, Fig. 4). On the arm is a hook upon which a watch may be conveniently hung near the thermometer. A second standard, with arm for support of the electric hammer for tapping the thermometer, may be adjustably attached to the main standard by a thumb-screw clamp. The current for igniting the iron wire over the substance to be burned in the capsule (O, Fig. 4) is conveyed by the rubber-covered wires (V, W), of which one is connected with the valve-screw of the bomb and the other with the insulated platinum wire (H) which passes through the cover.

Accessory Apparatus.

Apparatus for Moving Stirrer and for Igniting the Charge for Combustion.—The most convenient source of power for operating the stirrer we have found to be the direct or alternating current of the city electrical circuit, with suitable motors of about 1/20 horsepower. The same current serves to ignite the charge. As yet, no perfectly satisfactory substitute for these currents has been found. Six cells of the Edison-Lalande batteries have most nearly filled the requirements.

By means of a worm gear fastened directly to the armature

shaft of the motor, the speed is reduced, a final regulation being made, if necessary, by a rheostat, until the speed is such as to cause the stirrer to rise and fall about forty to fifty times per minute. With the apparatus as here described, it is important that the rate of stirring should not be less than 40 strokes (revolutions) to the minute. The connection between the motor and the stirrer is effected by means of a cord which is connected with the motor crank, passes upward to the ceiling or a shelf, over two pulleys, and thence down to the stirrer.

To heat the fine iron wire to incandescence, and thereby ignite the substance, requires a current of 3 or 4 amperes. If a 110-volt current is available, the necessary current may be obtained by switching it through four 32-candle power, 110-volt lamps in parallel. In case a 55-volt current is used, the 110-volt 32-candle power lamps would be replaced by a similar number of 16-candle power, 55-volt lamps. Lamps are especially desirable as resist-



Fig. 6.—Pellet press.

ances since they indicate to the observer whether the circuit is actually completed by the closing of the switch and whether it is broken by the fusion of the iron wire.

Pellet Press and Mould.—Solid materials to be burned are usually pressed into small pellets, so that they may easily be held in the small platinum capsule within the bomb. This pellet form is advantageous, also, in preventing the mechanical losses of loose material, which might occur either before or after ignition, and so insuring the complete combustion of all the material. The mold resembles an ordinary "diamond mortar". The press (Fig. 6) is

so constructed that a pressure of 50 pounds (22.5 kilos), applied at the extremities of the screw arm, gives a pressure of over 10 tons (9,100 kilos) on the pellet pin. In practice, such a pressure is rarely needed.

In molding a pellet, care should be taken to adjust the mold exactly under the screw of the press before turning the latter down and not to exert so great a pressure on the screw as to distort the pin and cause it to stick in the block. A little oil should be used between the end of the screw and the top of the pin, and both block and pin should be kept clean and free from grit. To remove the pellet, the screw is slackened, the mold slid out and inverted and the head of the pin pressed against the table. If the



Fig. 7.—Clamp and spanner.

pellet cannot be removed in this way, the mold may be placed again under the screw of the press with the projection at the base *at right angles* to the groove of the press. By turning down the screw, the steel disk can be made to drop into the groove and can be easily pushed aside so that the pellet can be forced out in the same way. With a few substances (especially cane-sugar) it is necessary to wash and dry the mold after making each pellet, as otherwise some of the finely powdered substance may adhere to the inner surface of the mold and make the pin stick. The press screw is closely fitted and care must be taken not to injure it by turning it down its full length with any force, as might be done, for instance, by setting it rotating rapidly when the mold is not in place.

Clamp and Spanner.—To hold the bomb securely, while the collar is being screwed down, a clamp or vise (Fig. 7) has been

devised, consisting of a fixed and a movable jaw enclosing a nearly cylindrical but slightly tapering space for the reception of the cup of the bomb. The jaws are drawn together through a maximum distance of about 0.5 cm. by a lever with a very coarse half-thread. A paper lining in the clamp will prevent the cup's slipping, and protect it from being marred. The spanner is about 1 meter in length and is provided with a steel pin of about 1 cm. diameter, which fits into a hole in the bomb collar. In using the spanner,



Fig. 8.—Appliances for filling the bomb.

care should be taken to fit the pin down its full length into the hole in the bomb collar; otherwise the edges of the hole may be worn away.

Bomb Support, Manometer, and Couplings for Filling Bomb with Oxygen from Oxygen Holder.—The oxygen used in this laboratory is furnished by the S. S. White Dental Mfg. Co., of Philadelphia, in cylinders about 125 cm. long and 18 cm. in diameter. These cylinders contain about 8 lbs., 8 oz., or 3850 grams oxygen, a quantity which should suffice for over 250 determinations. Brass coupling tubes are used to connect the cylinder with the manometer and with the bomb, which is supported, during the filling, upon a cast-iron shelf, as shown in Fig. 8.

The graduations of the manometer enable one to ascertain when

the supply of oxygen is nearly exhausted. When the pressure falls to 35 or 40 atmospheres, another cylinder of gas is ordered.

General Test of the Apparatus.

The general condition of the apparatus should be tested from time to time by check combustions. Benzoic acid and cane-sugar are convenient substances for this purpose, because they are easily obtained pure and their heats of combustion are accurately known (see p. 692). The benzoic acid has the advantage over the sugar that the pellets do not clog the pellet mold and that no kindler other than the iron wire is needed for the ignition.

II. METHOD OF USE OF THE APPARATUS.

Quantity of Substance To Be Used.

As explained below in the discussion of the accuracy of the method (p. 694), the quantity of material burned in the bomb should be such as will yield from 4000 to 7000 calories.

The following are suitable quantities of ordinary foods and feeding-stuffs:

Fats, oils, butter and very fat meats—as pork, fat mutton and fat beef.....	0.5 to 0.7 gram.
Leaner meats—as veal, fish, etc., and dried residue of milk.	0.7 to 1.0 gram.
Vegetable products consisting mostly of starch, sugar, cellulose, etc., with more or less of proteids and not much fat—as sugar, starch, flour, meal, potatoes, fruits, seeds of cereals, legumes, etc., fodders and feeding-stuffs, including hay, straw, meals, etc.....	1 to 1.5 gram.

Of substances which we have found convenient for tests of the accuracy of the determinations, the following are suitable quantities:

Naphthalene and camphor.....	0.5 to 0.7 gram.
Benzoic acid and hippuric acid.....	0.7 to 1.0 gram.
Cane-sugar and glycocoll.....	1 to 2.0 gram.

Preparation of the Material for Combustion.

Solids.—Solids in general are powdered and pressed into cylindrical pellets in the pellet mold as described above. The material is weighed approximately before, and accurately after, molding. Food samples are used ordinarily in the "partially dried condition". The methods followed in this laboratory in preparing such samples have been previously described.¹ Fatty sub-

¹ Report of preliminary investigations on the metabolism of nitrogen and carbon in the human organism, by W. O. Atwater, C. D. Woods and F. G. Benedict. Bull. 44, U. S. Dept. Agr., Office of Experiment Stations, 1897.

stances, such as dried milk, are weighed directly into the capsule without molding.

With some substances, special devices are required to secure ignition. A crystal of naphthalene serves as a kindler for such substances as sugar and glycocoll. The naphthalene may be inserted between two turns of the coiled iron wire with one edge touching the substance in the capsule. Or, instead of a coil, the wire may be formed into a loop, resembling one of the forms of wire office clips used for holding sheets of paper together, and the naphthalene placed in the loop, which should touch the substance in the capsule.

Substances which are still more difficult to ignite, *e. g.*; creatin and creatinin, may be enclosed in gelatin capsules, such as are used with volatile liquids (see below).

Fats, such as butter, may be ignited with naphthalene, or, preferably, by use of a small quantity of fibrous asbestos, such as is used in Gooch crucibles. The asbestos is placed on the fat in such position that the burning iron wire may fall upon it. In this way too rapid cooling of the wire is prevented, and local ignition of the fat ensured.

Oils.—Oils are absorbed in fibrous asbestos. The metal capsule is half-filled with asbestos, ignited in a Bunsen flame, cooled in a desiccator and is weighed before and again after addition of the oil.

Volatile Liquids.—Volatile liquids, *e. g.*, alcohol, may be enclosed in gelatin capsules.¹ We have found the "Beekman ideal" capsule No. 00, which weighs from 0.11 to 0.19 gram, very convenient for the purpose.

Urine.—The heat of combustion of urine cannot be satisfactorily determined by simply burning the solid residue, because a portion of the organic matter after carbonizing becomes encased in the fused ash and is thus protected from oxidation.² We have met with the same difficulty in attempting to burn urine dried on asbestos fiber according to the method used for the combustion of milk (see below). The difficulty is obviated by absorbing and drying the urine in cylindrical blocks of cellulose as proposed by Kellner.³ Suitable blocks are Carl Schleicher and Schüll's "No. 573" which are 15 mm. in height and 14 mm. in diameter and

¹ Berthelot uses collodion capsules for this purpose ("Traité pratique de calorimétrie chimique," p. 160).

² See Kellner: *Landw. Versuchst.*, 47, 296 (1896).

³ *Loc. cit.*

weigh about 0.7 gram. As the block and the dried urine are burned together, the quantity of heat due to the combustion of the cellulose must be estimated. It is scarcely practicable to determine once for all the specific heat of combustion¹ of the cellulose and to calculate from the weight of a block the heat that will be produced by its combustion, because the blocks contain varying quantities of moisture and are not easily dried to constant weight without danger of decomposition. If, however, a considerable number of blocks, say 50 or 100, are heated in the same drying oven at 95°-100° for three or four hours, they may then be assumed to have reached a uniform condition as to dryness and incipient decomposition. Determinations of the specific heats of combustion of three or four of the lot may, therefore, be made and the average result used for those burned with the urine. As the cellulose is very hygroscopic, the blocks should be kept in stoppered weighing bottles in desiccators over sulphuric acid and weighed in the same bottles. It is more convenient to have the weighing bottles large enough to hold several blocks.

The urine is prepared for combustion according to the following method, which was suggested by and is similar to that proposed by Tängl.² The weighed cellulose block is placed in an evaporating dish of 50 or 60 cc. capacity and the urine added from a 20 cc. pipette calibrated specially for urine.³ One or two pipettefuls, i. e., 20 or 40 cc., are taken according as the specific gravity is greater or less than 1.022. The weight of the urine is calculated from its specific gravity and the delivering capacity of the pipette. The urine is evaporated to dryness at 50°-60°. Repeated tests have shown that there is no appreciable loss of nitrogen in drying at this temperature. When dry, the block is transferred to the metal capsule and the urine residue remaining on the dish transferred to the capsule by wetting with water and wiping out with small quantities of fibrous asbestos held in bone-tipped forceps. After drying again at 50°-60°, the block is ready for combustion. The cellulose blocks will yield 2200-3000 calories each and the heat of combustion of urine ordinarily lies between 75 and 200 calories

¹ A convenient term for the heat of combustion per gram.

² *Arch. f. Physiol.*, Leipzig, 1869, Suppl. Bd., p. 251.

³ A pipetteful of urine is delivered into a tared weighing-bottle and weighed. The quotient of the weight by the specific gravity gives a value for the delivering capacity of the pipette. A number of such determinations are made with urine of different specific gravities and the results averaged. The results obtained with the urines of different specific gravities, though agreeing substantially among themselves, differ materially from that obtained by calibrating with water.

per gram, that of urine of specific gravity 1.022 being in the neighborhood of 110 calories. The heat set free in the combustion will, accordingly, vary from 4400 calories ($110 \times 20 + 2200$) to 7400 calories ($110 \times 40 + 3000$), and at least 50 per cent. of this will come from the combustion of the urine.

For drying the urine it is desirable to have a self-regulating oven. An oven surrounded by a water-jacket, provided with a mercury thermostat, serves the purpose admirably. It will be found advantageous to provide a shelf in the oven with perforations into which the metal capsules may be set.

A serious difficulty in the determining of the heat of combustion of the unoxidized material of urine is the tendency to decomposition of urea and perhaps other compounds by which more or less of the potential energy is set free. We have found the danger of such loss of energy from urine on standing to be much greater than might be suspected, nor have we yet found a convenient way for preserving it for any considerable time with certainty that no loss occurs. We have been in the way of adding about 5 cc. of commercial formalin to 800 cc. of urine, keeping it in a refrigerator and making the combustion as soon as possible.

The drying of urine *in vacuo* at room temperature, as elaborated by Cronheim,¹ is probably the safest course. Preliminary experiments, made a number of years ago in this laboratory, but not published, indicated the success of the method but the length of time required renders its use extremely difficult when a large number of samples are to be prepared.

Milk.—For the combustion of milk, a metal capsule of the largest size is loosely filled with fibrous asbestos upon which the milk is then absorbed and dried. About 5 grams of milk should be used and care should, of course, be taken to secure a representative sample.

About 20 to 25 grams may be taken from the supply, after thorough mixing, and placed in a small stoppered flask or other weighing-bottle, from which the 5-gram portions for the individual combustions may be weighed out. The milk in the weighing-bottle should, of course, be mixed by shaking immediately before each portion is poured out.

Milk may also be dried and burned on the cellulose blocks used with urine, but the asbestos method described above has two ad-

¹ "Conservierung des Harns für analytische und calorimetrische Zwecke," *Arch. f. Anat. u. Physiol., Phys. Abth., Sup.*, 1902, p. 262.

vantages. The correction for the combustion of the cellulose is avoided and the number of weighings is decreased.

Filling the Bomb.

The bomb cover being supported upon a ring-stand, the capsule containing the pellet is placed in position in the platinum ring. The ends of the coil of iron wire are wound around the vertical platinum wires (one turn only) and the coil adjusted so that it touches the substance to be burned but not the capsule. The naphthalene (if any is to be used) is placed in position. The cover is now placed on the bomb and a little oil dropped upon the top to prevent its turning with the collar, which is then screwed on and tightened by means of the clamp and spanner. The bomb is now ready to be filled with oxygen. With its valve slightly open, it is placed in position on the iron shelf (see Fig. 8) and connected with the manometer which is kept permanently connected with the oxygen cylinder. The valve of the oxygen cylinder is then opened cautiously. When the manometer indicates a pressure of 20 atmospheres, the oxygen is cut off, the bomb-valve closed, and the bomb disconnected from the manometer.

Leakage of gas from the bomb may occur either at the soft metal gasket (K) or at the conical tip of the valve-screw (F) (Fig. 2). Gas escaping at the gasket will usually make an audible sound. If the gasket is not too much worn, the leak may be stopped by screwing the collar tighter. A leak at the valve can be easily and quickly detected by placing the moistened finger over the opening (G). When the valve-tip or the conical shoulder into which it fits becomes corroded so that the valve cannot be closed by gentle pressure, it must be resealed carefully in a lathe to secure a proper fit. If, in filling the bomb, leakage occurs at L (Fig. 2), the cylindrical screw (E) should be tightened a little to press the packing (L) tightly around the valve-screw.

Arranging Apparatus for the Combustion.

The calorimetric water should now be put in the britannia-metal cylinder. Both the quantity and the temperature of this water are to be regulated. In order to facilitate the calculations, it is better to make the quantity always the same and such that the total hydrothermal value of the calorimeter system will be a round number, such as 2000, 2100 or 2200 grams. (Our custom is to make it 2100 grams.) In order to reduce to a minimum the correction for

the influence of the surroundings upon the temperature of the system, the water in the cylinder should be made cooler than the surroundings of the system (as measured by an ordinary thermometer placed in the inner air-space) by about the expected rise in temperature, or a little more. For example, if the quantity of substance to be burned is such as will yield about 6300 calories and the hydrothermal value of the system is to be 2100 grams, the rise expected will be 3° and the water in the cylinder should be made 3° - 3.2° cooler than the air of the inner air-space. The insertion of the bomb, which is at room temperature, will decrease this temperature difference by about one-sixth, the hydrothermal value of the bomb being about one-sixth that of the whole system, so that after the combustion the temperature of the system will be a little above that of the surroundings.

It is, obviously, more convenient to adjust the temperature of the water first and the quantity afterwards. The desired temperature can be readily obtained by mixing cooler water with that used in the preceding combustion (or with a portion of it). Water is then poured out of the cylinder until approximately the desired quantity remains; the cylinder, containing water and stirrer, is placed upon a tared balance, accurate to 1 gram, and small quantities of water are added or removed until the correct weight is obtained. The tare required is, of course, the desired hydrothermal value (*e. g.*, 2100 grams) minus the hydrothermal equivalent of the apparatus and plus the weight of the cylinder and stirrer.

The cylinder, containing stirrer and water, is now put in place inside the outer cylinders and the two conducting wires are joined, respectively, to the valve-screw and to the insulated conductor. The covers are put on and adjusted so that the stirrer will run smoothly, the thermometer is inserted and the stirrer set in motion. As soon as the different parts of the calorimeter system have assumed a common temperature, which usually requires two or three minutes, the mercury will begin to rise at a uniform rate, and the readings of the "initial" or precombustion period may begin.

The room temperature may have changed so much since the apparatus was last used that the thermometer must be reset. In that event, the water should be stirred a little after the insertion of the bomb and its temperature determined with an ordinary ther-

mometer, so that the actual temperature to which the zero of the reset thermometer corresponds may be known within half a degree.

Temperature Changes in the System.

If the calorimeter system were absolutely insulated thermally, only two temperature observations would be necessary for the determination of the heat of combustion of a substance. One of these could be made at any time after the system had come to internal temperature equilibrium after the insertion of the bomb and before the ignition of the substance, for the temperature would remain absolutely constant during this interval of time, whatever might be its length. This observation would give the *initial* temperature of the system. The second observation, that of the *final* temperature, could be made at any time after the heat from the combustion had distributed itself uniformly throughout the system, for then the temperature would again remain constant.

But it is, of course, impossible to insulate the system completely and, consequently, external influences are continually affecting its temperature. The most obvious and doubtless the most important of these external influences is the temperature of the medium surrounding the system. This medium may be regarded as made up of (1) the air of the inner air-jacket, (2) the walls of the inner indurated fiber cylinder, and (3) the air and walls of the outer air-jacket and the air of the room. Interchange of heat occurs between the system and (1) the air of the inner jacket by convection and radiation, (2) the indurated fiber cylinder by radiation, and (3) the air of the outer air-jacket and of the room by conduction through and convection by the rods of the stirrer. All of these interchanges may fairly be assumed to obey Newton's Law—that the rate of warming or cooling of a body is proportional to the difference of temperature between the body and the surrounding medium.

Less important external influences are (1) the production of heat by the friction and, in case of imperfect adjustment, by the impact of the stirrer, and (2) the evaporation of water from or condensation of water upon the system. The motion of the stirrer being regular, the quantity of heat produced by friction and impact (which is of course very small) is the same for any one minute as for any other. The amount of water condensed or evaporated during an experiment is without doubt very small in any case. At the same time it must be remembered that the latent heat of water

vapor at 20° being about 600 calories per gram, 1 calorie of heat is withdrawn from the system (and rendered latent) for every 0.0017 gram water evaporated. Conversely, the condensation of 0.0017 gram water upon the system would impart 1 calorie to it. Now, *condensation* can not occur at all except when the air of the inner air-space is so nearly saturated with moisture that its dew-point lies within 3° of its actual temperature, because the initial temperature of the calorimeter system is never more than 3° lower than the temperature of the surrounding air. The air of the inner air-space is practically completely enclosed by the inner fiber cylinder with its cover, so that very little air will diffuse in or out. Its volume is about 5.11 liters. This quantity of air, if saturated with moisture, would contain:

At 23° C.....	0.0204×5.11 gram. ¹
At 20° C.....	0.0171×5.11 gram.
Difference	$0.0033 \times 5.11 = 0.017$ gram.
Heat of vaporization.....	$0.017 \times 600 = 10$ calories.
At 30° C.....	0.0300×5.11
At 27° C.....	0.0255×5.11
Difference	$0.0045 \times 5.11 = 0.023$ gram.
Heat of vaporization.....	$0.023 \times 600 = 14$ calories.

If the initial temperature of the calorimeter were 27° (which is as high as it would be necessary to make it on a warm day in summer) and the air of the room (at 30°) were completely saturated with moisture, the quantity of heat imparted to the calorimeter by the condensation of all the moisture, from the air of the inner jacket would be 14 calories. In winter the initial temperature of the system does not exceed 20°, therefore the quantity of heat imparted to the system by condensation of moisture cannot be more than 10 calories. Moreover, even in the extreme cases now under consideration, the heat imparted to the system *during the experiment proper* will be very much less than the quantities mentioned, because the experiment proper is preceded by a "settling period" of at least two or three minutes and an "initial period" of five minutes, during which time the greater part of the moisture of the air will have been deposited and the dew-point will have fallen in consequence, so that the temperature of the system will have little more than begun to rise on account of the combustion of the substance in the bomb when it passes the dew-point of the air and

¹ See Smithsonian Phys. Tables, 2d ed., Washington, 1903, p. 135.

the deposition of moisture ceases. When we consider, further, how rarely the difference between the temperature of the air of a room and the dew-point will be as small as 3° , it is clear that the danger of error arising from the condensation of moisture upon the surface of the calorimeter system is insignificant.¹

Evaporation of water, involving abstraction of heat from the calorimeter system, will occur much more commonly. This will be a slower process than that of dew-deposition and it seems probable that the 5.11 liters of air in the inner air-jacket will not become saturated with moisture in the length of time required for a determination, and it may safely be assumed that the difference in the amount of evaporation per minute will not vary materially in the course of the fifteen or twenty minutes required for the completion of the observations necessary for the determination of a heat of combustion.

The correction for the "external influences" may, therefore, be estimated on the assumption that the rate of warming or cooling of the calorimeter system in a given minute is proportional to the difference between the average temperature of the system for that minute and the temperature of the surrounding medium. Further, the temperature of the surrounding medium may be regarded as constant. The correction for the effect of external influences on the temperature of the system may, therefore, properly be determined according to the method of Regnault, which is based upon the assumptions just mentioned. This consists in estimating the effect produced on the temperature of the system by the external influences during each minute of the time intervening between the ignition of the substance and the reattainment of internal temperature-equilibrium after the combustion ("main" or "combustion" period of the determination) from determinations of the mean

¹ It ought, perhaps, to be pointed out that this conclusion refers only to this particular form of apparatus. In calorimeters having no covers to separate the air of the air-spaces from that of the room, especially where by means of a water-jacket the temperature of the air-spaces is regulated so as to be always the same (whatever the temperature of the room), the question of dew formation may be of greater importance. Stohmann, when using his constant pressure calorimeter (in which, of course, the rise of temperature being more gradual than in a bomb calorimeter, the time during which dew deposition may occur is greater), endeavored to keep the temperature of the air-spaces constant between 17° and 18° and made the initial temperature of the system always about 16° . As the temperature was frequently lower than the dew-point of the atmosphere in summer, long interruptions of work were sometimes necessary in that season of the year (*J. prakt. Chem.*, 143, 22 (1887)). In his description of the method of use of the bomb-calorimeter, Stohmann again refers to the danger of dew formation and recommends that the difference between the initial temperature of the system and that of the surrounding air be not made too great (*J. prakt. Chem.*, 147, 519 (1889)).

temperature of the system during each minute of this period and of the mean temperature and the rate of change of temperature during two periods of five minutes each, one (the "initial" period) immediately preceding, the other (the "final" period) immediately following the main period. The correction is most readily calculated from the actual observations of the temperature of the system, made at the beginning and end of the initial and final periods and at intervals of one minute throughout the main period by means of the formula derived by Pfaundler (see p. 688).

The Thermometer Readings.—Readings may be begun at any time after the stirrer has been set in motion. They should be continued until there has been a *uniform* rise of temperature for five minutes, the differences between successive readings not varying by more than 0.002° . These five minutes constitute the initial or precombustion period.

Precisely at the end of the five minutes (*i. e.*, at the sixth reading of the initial period), the electric circuit through the fine iron wire in the bomb is completed by closing a switch. The resistance lamps are incandescent during the passage of the current and the extinction of their light indicates that the iron wire has been fused. This usually occurs within two or three seconds after the closing of the circuit. The switch should now be opened immediately to avoid error from the production of heat in the calorimeter by the passing of the current through the water.

Readings should be continued at intervals of one minute until the rate of fall of the mercury has become regular—an indication that internal equilibrium has been regained. This marks the end of the combustion period. In our routine work, however, we find it convenient, for the sake of uniformity in the calculations, to regard the combustion period as ending, in all cases, five minutes after the ignition. With an apparatus of the present model, it may safely be assumed that the system will return to equilibrium within five minutes, if the rate of stirring exceeds 40 revolutions per minute. After the final reading of the combustion period, the stirring is continued for five minutes (final or "post-combustion" period), at the end of which time another reading is taken.

Before each reading, the thermometer should be tapped with the electric hammer.

After the Combustion.

The bomb is now removed from the calorimeter and placed in

the clamp. After the pressure has been relieved by opening the valve, the collar is unscrewed and the cover removed. The interior of the bomb and the lining of the cover are rinsed with water and the rinsings titrated to determine the nitric acid (see below). The quantity of iron, if any, remaining unoxidized must be deducted from the quantity originally taken. It may be determined by weighing or (more conveniently) by measuring its length on a millimeter or other finely graduated scale.

Determination of the Nitric Acid.

The temperature in the interior of the bomb during the combustion is so great as to bring about the combustion of some of the atmospheric nitrogen left in the bomb on filling and also of some of the nitrogen contained in the substance burned. The product of this combustion is nitric acid. The heat produced by the combustion of the nitrogen is, of course, to be deducted from the total heat measured. For the determination of the nitric acid we follow Stohmann in using a solution of normal sodium carbonate (Na_2CO_3) of 3.706 grams per liter. One cc. of this solution contains 0.003706 gram sodium carbonate which is equivalent to 0.004406 gram nitric acid, the heat of formation of which is 1 calorie.¹ Thus each cubic centimeter of sodium carbonate used in the titration represents 1 calorie set free in the calorimeter by the combustion of nitrogen. Methyl orange is used as indicator.

Calculation of Results.

To find the heat of combustion of the substance under investigation, it is necessary to determine the total quantity of heat liberated in the apparatus and to deduct from this total the quantities due to the "accessory combustions" of the kindlers and the nitrogen. To determine the total quantity of heat liberated, one must know (1) the hydrothermal value of the calorimeter system, and (2) the rise of temperature reduced to true degrees and corrected for the influence of the surroundings. The details of the calculation can be best explained by an example.

The following copy of a page of our laboratory book gives the observations made in a determination of the heat of combustion of cane-sugar with the calculations therefrom, arranged in the form we have found most convenient. At the top of the page are given

¹ Molecular heat of formation of nitric acid from nitrogen, oxygen and water equals 14,300 calories. Berthelot: *Ann. chim. phys.*, (5), 6, 151 (1875); "Thermochimie," Vol. II, 107 (1897).

general data, such as the number and description of the sample, apparatus used, etc. Following this we have recorded the weighings of the sugar itself and of the iron wire and naphthalene and the titer of the nitric acid as found at the end of the determination.

SERIAL No.

Sample No.		Description, <i>Cane-sugar.</i>		Date, <i>July 13, 1901.</i>	
Bomb No. 3.		Observer, <i>J. F. Snell.</i>		Thermometer, No. 733.	
Capsule No. 1.		CORRECTION FOR ACCESSORY COMBUSTIONS.			
Wt. caps. + subs. = 4.2501		Wt. Fe 13.0 - 1.1 = 11.9 mgs. = 19.0 cal.			
Wt. capsule = 2.8783		Wt. naphthalene = 6.4 " = 61.6 "			
		HNO ₃ = 6.6 "			
Wt. substance, W = 1.3718		Correction for accessories = 87.2 "			
INITIAL PERIOD.	READ-INGS.	CORRECTED READINGS.	INITIAL PERIOD.		THERMOMETER CORREC-TION.
	1 1.018	1.015	Fall = - .014	T° air = 125.2	
	2 1.021		Rate V = - .0028	T° water = 23.8	
	3 1.025		1st reading = 1.0		
	4 1.027				
5 1.030	1.029	Meant°, $\theta = 1.022$	T° of zero = 22.8		
6 1.032			Corr. for 1° = + .001		
				Rise (degrees) = 2.6	
MAIN PERIOD.	7 2.300	2.3			Ther. corr. = + .0026
	8 3.650	3.7			
	9 3.678	3.7			
	10 3.662	3.7			
	11 3.653				
			CORRECTED READING, $\theta_1 = 3.646$ $\theta_2 = 1.029$	FINAL CALCULATION.	
			$\theta_1 + \theta_2 = 4.675$ $\frac{1}{2} = 2.3$	$\theta_1 = 3.646$ $\theta_2 = 1.029$ $\theta_1 - \theta_2 = 2.617$	
				Th. corr. = + .0026 Rad. corr. = + .0079	
				Corr. rise = 2.6275 " " $\times 2100 = 52.550$	
			FINAL PERIOD.	Total heat = 5517.8	
			Fall = + .013	Accessories = 87.2	
			Rate V' = + .0026	Corrected heat = 5340.6	
			V = - .0028		
			V' - V = + .0054		
				Log. corr. heat = 73485	
			Mean t°, $\theta' = 3.640$ $\theta = 1.022$	Log. W = 13729	
			$\theta' - \theta = 2.618$	59756	
				HEAT OF COMBUSTION PER GRAM = 3959	
FINAL PERIOD.	$\frac{\theta_1 + \theta_2}{2} = 2.3$				
	Sum = 15.7				
	5 θ = 5.1				
	Diff. = 10.6				
	Log. diff. = 0253				
	Log. V' - V = 7324				
	Colog $\theta' - \theta = 5820$				
	3397				
	Antilog. = + .0219				
	+ 5 V = - .014				
	Radia-tion cor-rection = + .0079				
	16 3.640 3.633				
	Time 3.30				
Remarks :					

Below the second horizontal line are given at the left of the page the thermometer readings. The last reading, No. 16, will be found near the foot of the page, below the calculation of the radiation correction. Corrections on account of variations in thermometer bore are applied to readings 1, 6, 11, and 16, and the corrected values given in the next column, with the exception of No. 11 (θ), which is placed for convenience in the third column and repeated in the fourth.

The total rise of the thermometer during the combustion period amounts to $3.646^\circ - 1.029^\circ = 2.617^\circ$ of the arbitrary scale of the thermometer (see Column 4, "Final Calculation"). To this "apparent" rise of temperature, two corrections are to be applied:

(1) The degrees of the arbitrary thermometer scale are to be reduced to true degrees (thermometer correction).

(2) Allowance is to be made for the influence of the surroundings upon the temperature of the calorimeter during the combustion period (radiation correction).

Thermometer Correction (Column 4).—The temperature of the water at the beginning of the combustion was 23.8°C . The reading of the calorimeter-thermometer corresponding to this temperature is 1° . The zero of the thermometer corresponds, therefore, to 22.8°C . At this temperature, 1° of the arbitrary scale of the thermometer is equal to 1.0010 true degrees. A correction of $+0.001^\circ$ is therefore to be made for each degree of apparent rise of temperature, or a total correction of $0.001 \times 2.6 = +0.0026^\circ$.

Radiation Correction (Columns 1-3).—During the early part of the combustion period, the calorimeter, i. e., the calorimeter system, is cooler than the surrounding air. The temperature is rising as the calorimeter system gains heat from the air. In the later part of the period, the calorimeter is ordinarily warmer than the air and its temperature is falling as heat passes from it to the air. According as the quantity of heat gained during the early part of the period is greater or less than the quantity lost later, the observed rise of temperature is greater or less than that properly attributable to the combustion and a subtractive or additive correction is to be made.

The correction is calculated by the Regnault-Pfaundler formula,¹

$$C = nV + \frac{V' - V}{\theta' - \theta} \left(\frac{\theta_n + \theta_o}{2} + \sum_1^{n-1} \theta - n\theta \right),$$

¹ Pfaundler: *Pogg. Ann.*, 129, 113 (1866).

where n = number of time units (minutes) in combustion period.

V = rate of fall of temperature of calorimeter during initial period.¹

V' = rate of fall of temperature of calorimeter during final period.²

θ = mean temperature of calorimeter during initial period.

θ' = mean temperature of calorimeter during final period.

$\theta_1, \theta_2, \dots, \theta_n$ = temperature at end of first, second, \dots n th minutes of combustion period.

θ_i = temperature at moment of ignition.

Applying this formula to our example, we find for the expression within the bracket 10.6° (see first column); for $V' - V$, 0.0054° , for $\theta' - \theta$, 2.618° and for nV , $5 \times (-0.0028) = -0.014^\circ$ (see middle column); whence $C = +0.0079^\circ$ (see first column).

Applying the thermometer and radiation corrections, we have $2.617 + 0.0026 + 0.0079 = 2.6275$ as the rise of temperature in true degrees (see "Final Calculation" in last column). The total hydrothermal value (water + hydrothermal equivalent of apparatus) being 2100 grams, the quantity of heat set free in the apparatus must have been $2.6275 \times 2100 = 5517.8$ calories.

Correction for Accessory Combustions.—The weight of the iron wire was 13 mg. The quantity unburned was 1.1 mg. The quantity burned was therefore 11.9 mg. The specific heat of combustion of iron being 1601 calories, the heat of combustion of 11.9 mg. is $11.9 \times 1.6 = 19$ calories. The quantity of naphthalene burned was 6.4 mg., which yields $6.4 \times 9.63 = 61.6$ calories, the specific heat of combustion of naphthalene being 9628 calories. The heat from the combustion of nitrogen as determined by titration of the nitric acid is 6.6 calories. The total heat from accessory combustions is therefore $19 + 61.6 + 6.6 = 87.2$ calories.

Deducting this quantity from the total heat set free in the apparatus, we have $5517.8 - 87.2 = 5430.6$ calories as the heat due to the combustion of the sugar. The quantity of sugar burned was 1.3718 grams. The specific heat of combustion according to this determination is therefore $5430.6 \div 1.3718 = 3959$ calories.

It will be found convenient to have tables mounted on cards,

¹ The change is actually a rise but for convenience in mathematical calculation it is here expressed as a fall in temperature. The value of V thus becomes negative.

² The change is generally a fall in temperature. Sometimes, however, the initial temperature of the water or the quantity of heat set free may be such that final temperature of the calorimeter will be lower than that of the surroundings, in which case there will be a rise of temperature and the value of V' will be negative.

giving the heat of combustion of quantities of naphthalene weighing from 4 to 10 mg. and of quantities of iron weighing from 10 to 20 mg. The weights may be expressed to tenths of milligrams and the heat quantities to tenths of calories. If iron wire of uniform diameter is used, the quantities of iron may be more conveniently expressed in lengths instead of weights. The specific heat of combustion of naphthalene is 9628 calories and that of iron 1601 calories.

Heat Unit.

The unit in which the heat of combustion, as thus calculated, is expressed is the quantity of heat necessary to raise the temperature of 1 gram of water 1° at the temperature which the water has in the determination in question. (In the above example it ranges from 23.8° to 26.4° .) Since the variations in the specific heat of water between 15° and 30° are small,¹ it scarcely seems necessary to correct results obtained at any ordinary room temperature for the variation of the specific heat of water from its value at 15° or 20° C. No error of any consequence will be committed, for instance, by taking 3959 calories as the determined specific heat of combustion of cane-sugar, whether the calories be defined as the heat necessary to raise the temperature of 1 gram of water from 15° - 16° or from 20° - 21° C.

Reduction to Constant Pressure.

The heat of combustion determined in the bomb calorimeter is that at constant volume, while the heats of combustion customarily

¹ The following table gives the results of determinations of the specific heat of water at 15° and 30° by different experimenters and different methods. The specific heat at 20° is taken as unity.

SPECIFIC HEAT OF WATER AT 15° AND 30° REFERRED TO THAT AT 20° .

Experimenter.	Method.	Specific heat of water.		Difference.
		at 15° .	at 30° .	
Bartoli and Stracciati ¹ .. .	Mixtures.	1.0005	1.0014	-0.0009
Ludin ²	"	1.0009	0.9999	+0.0010
Rowland ³	Frictional heating.	1.0014	0.9986	+0.0028
Griffiths ⁴	Electrical heating.	1.0014
Callendar and Barnes ⁵	"	1.0010	0.9987	+0.0023

¹ Bartoli and Stracciati: *Estratti dal Nuovo Cimento*, Series 3, Vol. 32. (1891). We have derived the figures from a table by Pernet in Louguine's *Bestimmung der Verbrennungswärme*, p. 18.

² Ludin: Inaugural Dissertation, Zurich, 1895. We have derived these figures also from Pernet's table.

³ As corrected by Waidner and Mallory, *Phys. Review*, 8, 232 (1899).

⁴ Value corrected by F. A. Wolff, Johns Hopkins Univ. Circular, June, 1898, cit¹¹⁴ by Waidner and Mallory, *Loc. cit.*, p. 235.

⁵ Callendar and Barnes: *Phys. Review*, 10, 213 (1900).

tabulated and used are those at constant pressure. To reduce the molecular heat of combustion of a solid or liquid compound, CaH_pNrO_q , at constant volume to that at constant pressure, it is necessary to add $(\frac{1}{2}p - q - r)T$ calories where T = the absolute temperature of the calorimeter.¹ To reduce the *specific* heat of combustion at constant volume to that at constant pressure the term to be added is, therefore, $(\frac{1}{2}p - q - r)T \div M$, where M = the molecular weight of the substance. For carbohydrates, this correcting term is zero, i. e., the heats of combustion at constant volume and at constant pressure are identical. For tripalmitin it amounts to + 15.6 calories, for tristearin to + 16.1 calories, and for triolein to + 15.2 calories. For protein it amounts to about + 3 calories.

With food materials in general, therefore, the heats of combustion obtained by the bomb-calorimeter should be increased by 15-16 calories for each gram of fat and by 3 calories for each gram of protein.

III. DETERMINATION OF THE HYDROTHERMAL EQUIVALENT OF THE CALORIMETER.

Now that the heats of combustion of many compounds are accurately known, the most convenient and satisfactory method for the determination of the hydrothermal equivalent of a bomb-calorimeter is to burn weighed quantities of such compounds in the bomb immersed in a known quantity of water.² From the observed rise of temperature and the known heat of combustion of the compound used, the total water value of the calorimeter system is calculated. Deducting from this the quantity of water used, we have the water value of the calorimeter itself.

The substances used in these determinations should be such as can easily be obtained pure and preserved without risk of change by deliquescence, oxidation, decomposition or otherwise. Their heats of combustion should have been determined in calorimeters whose hydrothermal equivalents have been learned by other methods.³ Those which have been determined by several investigators, independently and with closely accordant results, are to be preferred. Stohmann selected hippuric acid, benzoic acid, cane-

¹ See Berthelot : *Thermochimie*, 2, 30 (1897).

² Stohmann : *J. prakt. Chem.*, 187, 99 (1894).

³ For descriptions of such methods see Stohmann, Kleber and Langbein : *J. prakt. Chem.*, 147, 324 (1889); Berthelot : *Traité pratique de calorimétrie chimique*, 144ff.; Wiley and McGraw ; *This Journal*, 19, 439 (1897).

sugar and camphor as suitable for the purpose, these being substances for whose heats of combustion fairly accordant values had been obtained in his own laboratory and that of Berthelot. We have used substances of which we had specimens known to be pure from previous determinations of carbon, hydrogen and nitrogen and which were at the same time substances with regard to whose heat of combustion Stohmann and Berthelot were in approximate agreement. The substances happen to be the same as those recommended by Stohmann, except that we have used glycocoll instead of camphor.

Camphor, hippuric acid and benzoic acid are ignited directly by the heated iron wire but with cane-sugar and glycocoll a kindler (a naphthalene crystal) should be used.

The following are the specific heats of combustion of the five substances in question.

Stohmann used his own figures in preference to those of Berthelot. We have used the average.¹

	Stohmann.	Berthelot.	Tower. ²	Average.
Glycocoll	3129.1	3133.6	3131
Cane-sugar	3955.2	3961.7	3958.7	3959
Hippuric acid	5668.2	5659.3	5664
Benzoic acid	6322.3	6322.1	6322
Camphor	9291.6	9288.0	9290

In order to check the accuracy of the bomb, it is customary in this laboratory to make a combustion of cane-sugar about every two weeks. The average of the last twenty combustions thus made is 3959.3 calories per gram. The minimum result was 3948 and the maximum 3967.

If m be the number of grams of substance burned, q_1 the heat of combustion per gram, the quantity of heat liberated by the combustion will be mq_1 calories. If, at the same time, q_2 calories are produced by the accessory combustions of iron wire, of nitrogen and of kindling material (such as naphthalene), the total heat, q , set free within the calorimeter will be $q = mq_1 + q_2$; and if t be in degrees centigrade, the observed rise of temperature (corrected for thermometer calibration and for influence of surroundings of

¹ That Stohmann's methods of manipulation were more painstaking than Berthelot's is very plain to one who has seen both as actually carried out in their respective laboratories. At the same time, Stohmann's special refinements probably made but little difference in the actual results.

W. O. A.

² Unpublished experiments made in this laboratory.

calorimeter), w the weight of water used, and a the required hydrothermal equivalent, evidently $q = (w + a)t$, whence

$$a = \frac{q}{t} - w.$$

The method of calculation is illustrated by the following example:

	Substance.	Quantity burned. Grams.	Specific heat of combustion. Calories.	Heat liberated by the com- bustion Calories.
	Cane-sugar	1.0177	3959	4029.0
	Iron	0.0201	1600	32.2
Accessories {	Naphthalene	0.0078	9628	75.1
	Nitrogen (by titration of the nitric acid formed)			6.0
	Total heat liberated, q			4142.3
	Corrected rise of temperature, t			1.9751°
	Weight of water used in calorimeter, w			1685 g.

whence, $a = \frac{4142.3}{1.9751} - 1685 = 412$ grams.

A number of determinations (at least three) of a are made in this way with each of three or four substances. The triplicate results with each substance should agree very closely with each other as should the several averages of these triplicates. If the latter do not differ by more than a few (*e. g.*, 5) grams, the average of these averages may be taken as the correct hydrothermal equivalent of the calorimeter.

To insure that the hydrothermal equivalent thus obtained shall be actually that of the apparatus as used subsequently for determinations of heats of combustion, the quantity of water used in the calorimeter in the determinations of the hydrothermal equivalent should be as nearly as possible the same as in the regular determinations. In the above example, for instance, 1685 grams of water were used, because we knew that the hydrothermal equivalent was not far from 415 grams and it was our intention to have regularly a total water-value (water + hydrothermal equivalent) of 2100 grams.

A tolerably close estimate of the hydrothermal equivalent may be made in advance of the accurate determinations by calculation from the weights and specific heats of the *materials* of which the calorimeter is constructed, only those parts being taken into account which share the temperature rise of the water. These are,

of course, the water cylinder, the lower parts of the thermometer, the lower part of the stirrer, and the bomb with its contents. A statement of the weights of the component materials is furnished with each of the calorimeters here described. The following are the specific heats as nearly as we know them:

	Material.	Sp. heat.	Source of figures.
<i>Bomb:</i>			
	Tool steel.....	0.1087	Determined by Dr. Tower.
	Hotchkiss gun steel.....	0.1114	" " " "
	Platinum.....	0.032	{ Smithsonian Phys. Tables, 2nd ed., Washington, 1903, p. 296.
	Lead.....	0.030	{ Smithsonian Phys. Tables, 2nd ed., Washington, 1903, p. 296.
	German silver.....	0.094	{ Tomlinson: Proc. Roy. Soc., 1885.
	Oxygen (constant volume).....	0.157	{ Wüllner, "Experimental Physik," (4th ed.), III, 509.
<i>Water-cylinder:</i>			
	90 pct. tin.....	0.054	Smithsonian Phys. Tables.
	Britannia-metal { 7 pct. antimony.....	0.049	" " "
	3 pct. copper.....	0.092	" " "
<i>Stirrer:</i>			
	Brass.....	0.094	Kohlrausch, Phys. Meas.
<i>Thermometer:¹</i>			
	Mercury.....	0.033	Smithsonian Phys. Tables.
	Glass.....	0.19	Kohlrausch, Phys. Meas.

IV. ACCURACY OF THE METHOD.

Theoretical Discussion.

If m be the quantity of substance burned, $h = a + w$, the hydrothermal value of the calorimeter system, a being the hydrothermal equivalent of the apparatus and w the weight of the water, and t the rise of temperature of the system due to the combustion; then the specific heat of combustion of the substance, $q = \frac{ht}{m}$.

From this formula it is clear that errors making h or t too large or m too small will make q too large in the same proportion, and errors making h or t too small or m too large will make q too small in the same proportion. An error in a , the hydrothermal equivalent of the apparatus, will affect equally all determinations made with that apparatus, *i. e.*, will produce the same percentage error in each. Errors in m , w , or t , on the other hand, will affect only the individual determination.

¹ We have found by examination of a broken Fuess thermometer of the kind used in this laboratory and described above, that the portion immersed in the calorimeter water consists of about 8.5 grams glass and 32.5 grams mercury.

Allowing a possible error of ± 0.0002 grains in weighing the substance, we have a possible error in m and therefore also in q of ± 0.02 per cent. when 1 gram, or of ± 0.04 per cent. when 0.5 gram is used. Allowing a possible error of ± 1 gram in the weighing of the water, the possible error in h , leaving out of consideration the constant error in a , is ± 0.05 per cent. on a hydrothermal value of 2100 grams. The possible error due to t will, however, be greater. $\pm 0.001^\circ$ must be allowed on each reading of the thermometer or $\pm 0.002^\circ$ on the two readings necessary to determine a temperature difference. In addition, the correction for the influence of the surroundings upon the temperature of the calorimeter is uncertain. If we allow another $\pm 0.002^\circ$ (which is probably a liberal estimate) for error here, we have a possible total error of $\pm 0.004^\circ$. In the measurement of temperature differences of from 1° to 4° , the maximum errors, on the above assumption, will be from 0.4 to 0.1 per cent.

It is clear, then, that for accurate results the greatest care is needed in the temperature measurements. To secure this accuracy:

(1) The quantity of substance burned should, if practicable, be large enough to give a rise of from, say, 2° to 3.5° . In other words, if the water-value of the calorimeter be made 2100 grams, a quantity sufficient to yield 4000 to 7000 calories or a little more should be used.

(2) The thermometer must be accurate and must be accurately read and corrected.

(3) The temperature of the air-space immediately surrounding the metal cylinder should be kept constant throughout each experiment so that the conditions may be correct for the application of the Regnault-Pfaundler "radiation correction" (see above). So far as we are aware, the most accurate experimenters in this field work in rooms of constant temperature, and some protect their calorimeters from radiation from the observer's body by enclosing them in metal cylinders having double walls with interspaces filled with water. According to our experience, however, the two insulated fiber cylinders of our calorimeter afford sufficient protection, and reasonably accurate determinations may be made in an ordinary laboratory room, provided the temperature is nearly constant during each experiment. We have, however, arranged a small room in the center of the basement of our laboratory for this special work.

Accuracy of Actual Determinations.

In the actual use of the apparatus, the accuracy attained is about what would be expected from the foregoing considerations. Thus, in thirteen determinations of the heat of combustion of benzoic acid, made by three observers in this laboratory, the average deviation of the individual results from the mean was ± 0.16 per cent. and the maximum deviation -0.35 per cent. The minimum quantity of substance burned being 0.8 gram, we should anticipate a possible error of ± 0.03 per cent. in the weighing. The minimum rise of temperature produced in the calorimeter being 2.5° , we should look for a possible error of ± 0.16 per cent. in the determination of the temperature difference. Allowing a possible error of ± 0.05 per cent. in the weighing of the water and leaving out of consideration personal error and error due to the use of different apparatus, we should expect to find a maximum error of $0.03 + 0.16 + 0.05 = \pm 0.24$ per cent. in the individual results. The actual maximum error was, as just stated, -0.35 per cent. The difference barely exceeds that between the specific heat of water at 15° and at 30° (see p. 690, foot-note).

That, in general, the actual determinations on solids and homogeneous liquids have very nearly theoretical accuracy is shown by the following comparison of anticipated errors, estimated in the manner just illustrated, with the actual deviations of the results of individual determinations from the average of those results.

Substance.	No of determinations.	No. of samples.	No. of observations.	Maximum error.		Mean error. Actual. Per cent.
				Anticipated. Per cent.	Actual. Per cent.	
1. Benzoic acid.....	13	..	3	± 0.24	-0.35	± 0.16
2. Hippuric acid.....	9	..	3	0.31	-0.39	0.22
3. Cane-sugar	18	..	4	0.38	$+0.51$	0.28
4. Cellulose blocks.....	15	5	3	0.38	$+0.43$	0.17
5. Commercial oils.....	84	40	1	0.29	$+0.39$	0.12
6. Beef.....	8	4	2	0.23	± 0.20	0.07
7. Dried residues of milk..	8	4	1	0.22	± 0.14	0.11
8. Other foods of animal origin, <i>e. g.</i> , butter, pork, casein	10	5	2	0.29	± 0.20	0.09
9. Vegetable foods and fodders, largely carbohydrate in composition..	14	7	2	0.27	± 0.18	0.10
10. Human feces.....	10	5	3	0.24	± 0.25	0.12

This comparison indicates pretty clearly, we think, that with substances of these classes, there cannot be any very important sources of error other than those discussed above, also that the allowance of $\pm 0.002^\circ$ for uncertainty in the radiation correction is ample.

From the table, it would appear that the determinations on substances of mixed composition were actually more accurate than those on pure chemical compounds. The explanation of this is, doubtless, partly that in the case of the substances of mixed composition, the quantities burned were such as to set free larger quantities of heat, thus reducing the anticipated maximum error, and partly that on these substances the duplicate or triplicate determinations on each sample were made by a single observer with a single apparatus, while the determinations on benzoic acid, hippuric acid, cane-sugar, etc., were made by more than one observer with more than one apparatus.

With a substance of uniform composition, combustible without the aid of a kindler, it is a safe practical rule, in case only two determinations are ordinarily made, to make an additional determination whenever the duplicates vary from each other by 0.5 per cent. or more (*i. e.*, from their average by ± 0.25 per cent. or more) and in case three or more determinations are made, to reject results varying from the average by over ± 0.4 per cent.

Where a kindling substance is used, especially when, as in the combustion of urine on cellulose blocks, the kindler furnishes a considerable proportion of the total heat measured, greater latitude between duplicates must be allowed and lower accuracy of result accepted. If 20 cc. of urine (a little over 20 grams), having a specific heat of combustion of 110 calories, be burned with a cellulose block yielding 2200 calories, the maximum error anticipated will be ± 0.4 per cent. in the determination of the temperature difference and about ± 0.2 per cent. due to the use of the kindler, or about ± 0.6 per cent. in all. Duplicates varying by less than 1.2 per cent. should, therefore, not be rejected, but an additional determination should be made in case the duplicates differ by over 0.5 per cent.

With milk, owing to the great difficulty of taking uniform samples, the variations between duplicates sometimes amount to 2 per cent. or more. Where such wide differences occur, a third determination is obviously necessary, but until a better method of

sampling milk is devised, we must be content to accept less accurate results with this substance than we are able to obtain with solids and with liquids of uniform composition.

Verification by the Respiration Calorimeter.

Experimenters with the bomb-calorimeter have felt the lack of an absolute standard for verification of the accuracy of the results obtained by its use. Such a verification is found in comparative measurements of the heat of combustion of alcohol by the bomb-calorimeter and by the Atwater-Rosa respiration calorimeter¹ in this laboratory.

To establish the accuracy of this latter apparatus as a calorimeter, known amounts of heat are introduced electrically, and are measured by the apparatus. In the average of a large number of determinations, the disparity between the amounts introduced and the amounts as measured has been about 1 part in 10,000.

The accuracy of the apparatus for the determination of heat being thus shown, considerable quantities of alcohol are burned in the respiration chamber during long periods (about 40 grams per hour during periods of twelve to one hundred hours each) and the heat thus produced is measured and the heat of combustion per gram of alcohol is determined. Aside from the possibility of a slight error in the figure 0.592, which was employed for the latent heat of evaporation of water, it seems hardly probable that there can be any considerable error in the average of the results obtained. Omitting from consideration the experiments in which obvious disturbing factors influenced the results, and considering only the experiments of the past three years, during which earlier errors of various kinds were eliminated, eleven series of experiments performed during the years 1900-2 gave figures for the heat of combustion of alcohol which averaged 7090 calories per gram. The maximum and minimum figures were 7111 and 7048 respectively, the range of error being thus ± 0.6 per cent. The average of six determinations with the bomb-calorimeter, corrected for constant pressure, was 7.095 calories, the maximum and minimum being 7110 and 7068 respectively, and the range of error ± 0.4 . In other words, the average of the determinations with the bomb differs from that with the respiration calorimeter by only 0.07 per cent.

¹ U. S. Dept. Agr., Office of Experiment Stations, Bulletins 63, 69 and 109.

We thus have a standard to which the determinations by the bomb-calorimeter are referable and which shows them to be correct.

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PETROLEUM IN CALIFORNIA.

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Received February 9, 1903.

WITHIN the last few years California has developed a new industry, that of petroleum. The knowledge that it existed is not new. Seepages occur in various parts of the State, and natural gas is found over a very large area. Immense deposits of asphaltum occur in the southern counties and were used by the early Mission Fathers. Attempts were made to distil the crude oil and in 1855, Pico erected a small refinery.

The discovery of oil in Pennsylvania produced great excitement, not only in the east but in California. Claims were located in all parts of the State and companies formed to work them. In 1865 there were sixty-five companies in existence with a nominal capital of \$45,000,000. Oil properties were exploited in every county from Humboldt to San Diego, but there was no apparent success, owing to lack of prospecting, insufficient depth of wells, and to the opinion of eminent chemists and geologists that the oil would not be found in large quantities, and could not be refined.

Petroleum occurs in every part of the State, but as yet only the southern part yields any large quantity. Ventura, Los Angeles, Orange, Santa Barbara, Kern and Fresno Counties furnish practically all the oil that is produced, although in many other counties small yields have been obtained.

Los Angeles, in common with other districts, was exploited nearly forty years ago, but no oil was obtained. The wells were not bored deep enough. Nothing further was done for thirty years, until in 1892 a well 365 feet deep was sunk and yielded oil. In three years, more than 300 wells were drilled and most of them yielded oil. Other districts in the neighborhood were exploited, and hundreds of new wells located. The production of oil rapidly increased until in 1897 it had reached 1,400,000 barrels. The total amount of oil obtained from the Los Angeles district amounts to more than 9,000,000 barrels. About 1400 wells have been dug,

none of them very deep. The oil sand averages about 60 feet in thickness. A second sand has been worked with profit, and it is believed that a third sand exists.

Other districts in Los Angeles County have been worked for oil, the principal ones being Whittier, Fullerton and Puento. This oil is usually light in gravity, so much so that the most of it is distilled and only the residuum used for fuel. In Ventura County there are more than 500 wells, over 300 of them being worked now; they are from 500 to 2000 feet deep. Practically all are owned by the Union Oil Company. In Santa Barbara County, oil seepages have long been known. In 1895 some wells were dug on the beach at Summerland, and oil was struck at the depth of only 125 feet. The deepest are only about 400 feet. Since then more than 300 wells have been bored, some on the beach and some on the ocean, 400 to 1200 feet from the shore. Some of the wells in other districts are 1000 or more feet deep. The oil is heavy, averaging about 14° Bé. The yield is between 8000 and 10,000 barrels a month but has been much more. The Fullerton and Brea districts in Orange County produced last year over 1,000,000 barrels. The oil varies greatly in gravity, from heavy, 14° Bé., to as light as 35° Bé.

North of the Tehachapi, the whole valley of the San Joaquin seems to be underlaid with oil, although as yet only a small area is worked. The principal fields are in Fresno and Kern counties. In Fresno County is the well-known Coalinga district. This field is limited in extent, extending over but a few sections, but in this area there are very many wells. Some are very deep, one being 2300 feet. The oil is of different qualities, some very heavy and black in color, others very much lighter, about 35° Bé. There are two pipe lines to transport the oil to the railroad, and a pipe line to the ocean is about to be commenced.

Another district in Fresno that has produced some oil is Kreyenhagen, 22 miles southeast of Coalinga. Like Coalinga, it produces two qualities: one green and light, 35° Bé., and one black and heavy, 14° Bé. Other districts have been prospected but they yield little or nothing.

In Kern County we come to the largest field that has yet been discovered. It has developed marvelously, over 600 wells have been dug and nearly all are producers. Some of them yield only a few barrels a day but most of them are about 50-barrel wells.

Some have produced much more: 200, 400 or even 600 barrels a day. None of them are flowing. The average depth of the wells is about 800 feet; some are less than 500 feet, and the deepest are less than 1100 feet. The oil is thick, black and heavy, ranging in gravity from 9° Bé to 22° Bé, usually being from 14° to 17° Bé. It usually carries much fine sand, from which it is freed by settling. The oil is sometimes previously thinned by heating with steam. The oil carries large amounts of asphaltum, from 10 to 40 per cent. The present well-defined producing area of the Kern River district measures about 5 miles long and 3 miles wide, the longer axis extending in a northwesterly direction, and the thickness of the oil sand varies from 50 to 400 feet, a large proportion being of the latter depth. The limits of the field have probably not been reached, and in time the producing area will probably be enlarged. 20,000 to 25,000 barrels a day are shipped from this district, and this yield could be increased many fold, if there was a sufficient demand. Owing to the lack of demand and consequent low price of oil, many of the wells are not pumped, the owners waiting for better prices. A pipe line is being constructed by the Standard Oil Company from Bakersfield to their refineries at Point Richmond on San Francisco Bay, a distance of 280 miles. The pipe is 8 inches in diameter, covered with asbestos and buried. The reason for this is that the oil is so viscous at ordinary temperatures that it cannot be pumped. It must be heated, and at every pumping station, which are 27 miles apart, a heating plant is installed. The company has also built 100 37,500-barrel storage tanks at Bakersfield and two 75,000-barrel cement reservoirs. The large area of the field and the great thickness of the oil sand indicate that the life of the wells will be very long. The Kern River field is the most important in California and produces more than half the entire yield of the State.

Another part of Kern County where petroleum is found is the McKittrick district. Here are large deposits of asphaltum that are worked by the Southern Pacific Railroad. They have built a branch 65 miles long, terminating at Aspalto. This district contains a few good wells, but many are useless. Some give very large amounts of water. The oil is light, about 33°, and the yield is about 50,000 barrels a month. A third district in Kern County is the Sunset. This has also been worked for asphaltum for nearly ten years. It has lately been developed for oil. Over fifty

companies are operating; some have good wells, as much as 100 barrels a day, but most of them are barren. Nearly all are troubled with fine sand that caves in and chokes the wells and also remains in the oil. There is a great lack of water. What there is is usually salt or alkaline. Most of the oil is heavy, containing about 30 per cent. to 40 per cent. asphaltum of good quality. The asphaltum for a time was more valuable than the oil, owing to the lack of transportation. This has been remedied by the railroad building a branch line connecting at Bakersfield. The adjoining Midway district appears promising but as yet has not produced much.

The foregoing are the districts that produce practically all the oil in California. But it has been found in greater or less quantity in almost every county, and also in parts of Oregon, Washington, British Columbia and as far north as Alaska. Some of the counties in which prospecting has been carried on extensively are, all the southern counties and in San Benito, Monterey, Santa Clara, San Joaquin, San Mateo, San Francisco, Alameda, Contra Costa, Napa, Sonoma, Colusa, Tehama, Mendocino, Humboldt and Shasta Counties. Occasionally the wells have been bored very deep. Some in Contra Costa and San Mateo are 1200 feet deep. There is a well in Humboldt in the Mattole district over 2000 feet deep. They have all yielded a small amount of oil, but there are no wells that give more than a few barrels a day. The oils along the coast from Santa Clara northwards in San Mateo, Mendocino and Humboldt Counties, and eastward to Colusa County, are very different in quality from the southern oils. They are lighter in color—usually yellow—lighter in gravity, varying between 19° Bé. and 40° Bé., and contain a paraffin residue, with little or no asphaltum.

To recapitulate, we find that oil is distributed over this entire western coast, but as yet practically the whole amount produced comes from a few districts in the southern part of California. The following table compiled by Mr. C. L. Yates for the State Mining Bureau, will illustrate this.

The statistics for last year have not been accurately compiled, but the total amount produced will be 13,000,000 barrels. In spite of this greatly increased supply, the price is gradually rising, and when the present long-term contracts have expired, the price will probably go still higher.

The method of boring wells is practically the same as used in

PETROLEUM PRODUCTION OF CALIFORNIA FROM 1897 TO 1901.

County.	1897.			1898.			1899.			1900.			1901.		
	Product. Bbla.	Value.	Product. Bbla.	Value.	Product. Bbla.	Value.	Product. Bbla.	Value.	Product. Bbla.	Value.	Product. Bbla.	Value.	Product. Bbla.	Value.	Value.
Fresno.....	70,140	\$ 70,840	154,000	\$ 154,000	439,372	\$ 439,372	547,960	\$ 547,960	525,433	\$ 525,433	525,433	\$ 525,433	525,433	\$ 525,433	\$ 236,444
Kern	10,000	10,000	15,000	13,500	919,275	827,348	3,902,125	1,131,616	3,902,125	1,131,616	3,902,125	1,131,616	1,131,616
Los Angeles...	1,327,011	1,327,011	1,462,871	1,462,871	1,409,356	1,409,356	1,722,887	1,722,887	2,304,432	1,062,038	2,304,432	1,062,038	2,304,432	1,062,038	1,062,038
Orange ..	12,000	12,000	60,000	60,000	108,077	108,077	254,397	254,397	302,652	181,591	302,652	181,591	302,652	181,591	181,591
Santa Barbara .	130,136	130,136	132,217	112,549	208,370	191,288	183,486	165,138	203,616	113,385	203,616	113,385	203,616	113,385	113,385
Ventura.....	368,282	368,282	427,000	571,000	496,200	496,200	443,000	398,700	472,087	236,028	472,087	236,028	472,087	236,028	236,028
Miscellaneous .	4,000	10,000	3,000	6,000	1,500	3,000	248,945	236,498
	1,911,569	\$1,918,269	2,249,088	\$2,366,420	2,677,875	\$2,660,793	4,329,980	\$4,152,928	7,710,315	\$2,961,101	7,710,315	\$2,961,101	7,710,315	\$2,961,101	\$2,961,101

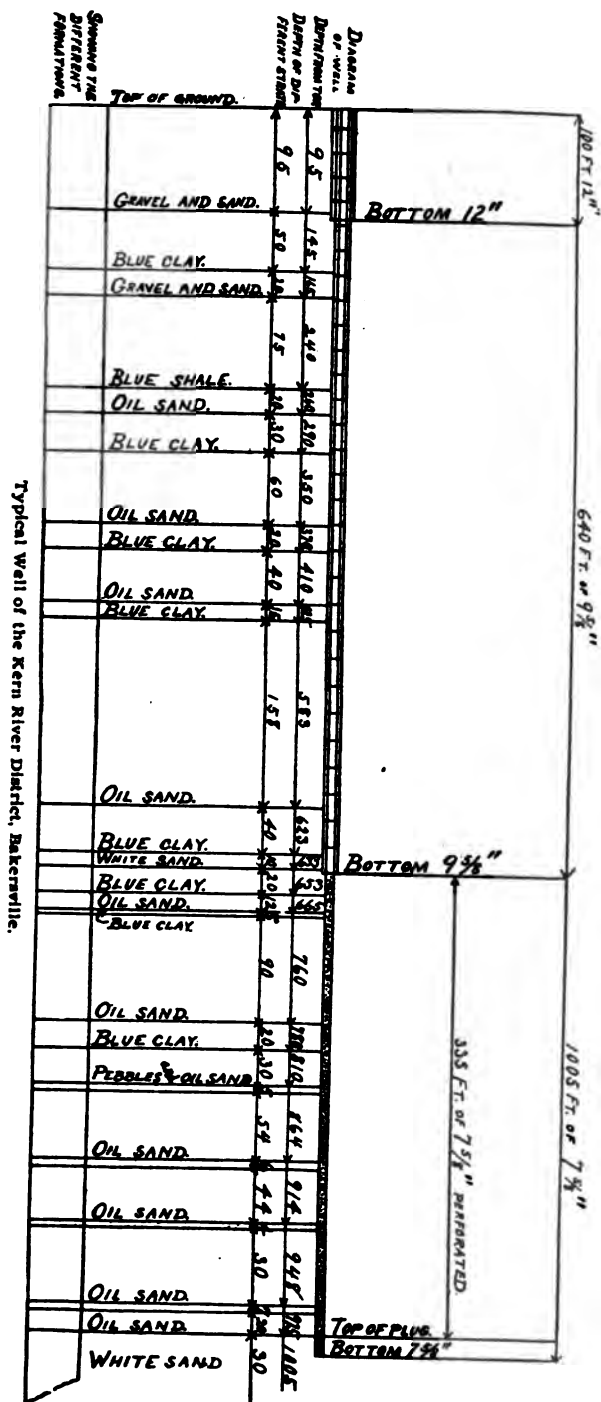
the east. The character of the formations passed through varies greatly according to the district. As the Kern River district is the largest, the following diagram showing a typical well is given.

There is apparently much difference in the quality of California petroleums obtained from different localities, but actually they are very much the same. The differences probably result from natural distillations or filtrations, a lighter oil being obtained, leaving a heavy residue containing asphaltum. Extreme variation is from 10° Bé. for oils of the McKittrick and Sunset district; to 35° Bé. for Coalinga and Puento. A water-white oil is found in the Newhall district that has a gravity of only 50° Bé. and leaves scarcely any residuum. It is evidently a natural filtrate or distillate. San Mateo, Colusa and Humboldt oils are apparently very different from most of the others, as they apparently contain little or no asphaltum. They have a gravity of from 17° to 50° Bé.

Chemically considered, California petroleums seem to be intermediate between Eastern and Russian oils. They contain paraffins, benzenes and naphthenes. Most of them contain nitrogen and sulphur. The sulphur seems to be contained in a volatile body, and is frequently almost entirely removed in a fraction boiling between comparatively narrow limits.

The chief use of California crude petroleum is for fuel. Many of the large steam plants have discarded coal and now burn oil. The annual consumption of coal in California has been nearly 2,000,000 tons, and nearly half of this has been displaced by oil. Crude oil in bulk does not burn readily, especially if it is heavy. A special form of burner must be used. The usual method is to inject the oil in a very fine spray, by means of steam, and the heated, finely divided particles will burn easily and completely.

As the flame is exceedingly hot, it is directed on to brickwork on the bottom of the fire-box, and the boiler heated to a large extent by radiation. The intense heat is wearing on the boilers, but the advantages of oil over coal, especially on this coast, are many. It is more convenient to handle,—it is cleaner and it is cheaper. The liquid oil is transported much more easily than the solid coal. When properly burned, there is no smoke or soot or cinders. There are no ashes, so the boiler tubes do not get stopped up. Oil-heating is particularly desirable for locomotive engines. Ease of loading and firing and absence of cinders, with consequent comfort to passengers, and no danger of setting fire to grain fields or



Typical well of the Kern River District, Bakersville.

fences, are self-evident advantages. In Russia, nearly all the locomotives are thus run. Many of the engines in this state are oil burners, and it is only a question of time when practically all will be altered. The cheapness depends partly on the relatively greater economy in handling and partly on the greater heating value as compared with coal. Seven barrels of oil will weigh about a ton; at a cost of \$1.25 per barrel, this would be equivalent to \$8.90 per ton; at \$1.50 per barrel, \$10.50 a ton. But the heating value of oil, weight for weight, is greater than that of coal. From a number of experiments we have made in our laboratory, we find that the heating value of California oil is between 10,000 and 11,000 calories, averaging about 10,500. The best coals of this coast average 7,000 to 8,000 calories, and the usual steam coals much less. Comparing the cost of coal and oil at the above prices as to the theoretical heat value, a ton of oil would be worth \$6.00 to \$8.00 and the coal \$8.00 to \$9.00. The actual difference is very much greater than this, as there is much less waste in oil heating. From many actual experiments made under boilers, it has been found that from 4 to 4½ barrels of oil is equivalent to one long ton of good coal, a saving of from 25 per cent. to 40 per cent., so that coal cannot compete with petroleum at the present prices nor can it until its cost is reduced to between \$4.00 and \$5.00 a ton, whereas it is between \$7.00 and \$8.00 a ton, and the best qualities bring from \$10.00 to \$14.00. Oil is selling in San Francisco now at less than 70 cents a barrel. This brings the cost of fuel on this coast to a par with the cost in the east, with its consequent great advantages. The smelters around the bay are using oil with a saving of over 50 per cent. in the cost of fuel.

Outside of fuel, crude petroleum is used to a slight extent on this coast in gas-making, as a coarse lubricant and as an insecticide in the orchards. A comparatively small amount is thus consumed. The Elmore process for concentrating ores, which employs petroleum, may consume a quantity.

The refining of oil is conducted on an increasing scale. Thirty-three refineries are now in operation. The capacity varies from 50 to 2000 barrels a day, the aggregate amounting to from 8000 to 10,000 barrels daily. The usual distillates are made—benzines, illuminating and lubricating oils. None of these except the benzines are of very good quality. They are used chiefly to mix with eastern oils.

PHYSICAL CHARACTERISTICS OF CALIFORNIA PETROLEUMS.

Serial No.	District.	Color.	Gravities temperature. °C.	Corresponding °F.	Flashing-point. °C.	Burning-point. °C.
54	Los Angeles.	Black.	0.9589 at 15.0	16.1	115.5	134.0
116	Whittier.	"	0.9397 "	19.3	73.0	80.2
87	Ventura.	"	0.9460 " 22.0	18.3	73.0	80.2
155	"	"	0.9890 " 11.0	11.6	73.0	80.2
50	"	"	0.9143 " 18.0	23.6	73.0	80.2
186	"	Brown.	0.9159 " 15.0	22.8	73.0	80.2
93	Newhall.	0.9159 " 15.0	22.8	73.0	80.2
156	Kern.	Water-white.	0.8059 " 19.0	45.0	73.0	80.2
157	"	Black.	0.9372 " 18.5	15.7	73.0	80.2
111	"	"	0.9533 " 20.3	15.9	73.0	80.2
112	"	"	0.9760 " 18.0	13.5	73.0	80.2
134	McKittrick.	"	0.9651 " 18.1	15.1	73.0	80.2
135	"	"	0.9458 " 18.0	18.5	73.0	80.2
103	Sunset.	"	0.9628 " 18.0	15.4	73.0	80.2
85	"	"	0.9589 " 17.0	16.2	73.0	80.2
149	Summerland.	"	0.9245 " 18.0	22.0	73.0	80.2
147	"	"	0.9815 " 21.0	12.7	73.0	80.2
160	Coalinga.	Brown.	0.9792 " 21.0	13.0	73.0	80.2
52	"	"	0.9276 " 21.1	21.4	70.0	94.0
51	"	"	0.8962 " 26.2	27.0	70.0	94.0
159	Santa Clara.	Light brown.	0.9493 " 17.4	17.9	70.0	94.0
184	San Mateo.	Brown.	0.8515 " 18.0	34.4	89.5	104.0
127	Santa Cruz.	Black.	0.9206 " 15.0	22.6	90.0	102.0
100	Napa.	Brown.	0.9565 " 18.0	16.8	131.0	138.0
98	"	Dark brown.	0.9603 " 18.0	16.0	131.0	138.0
154	Colusa.	Yellow.	0.9655 " 18.0	15.1	135.0	140.0
142	Contra Costa.	Black.	0.8229 " 19.0	40.0	135.0	140.0
161	Humboldt.	Red-brown.	0.9533 " 17.0	15.1	135.0	140.0
94	"	Yellow.	0.8810 " 15.5	28.9	135.0	140.0
95	"	"	0.8992 " 18.0	26.3	135.0	140.0
96	"	"	0.8951 " 18.0	27.0	135.0	140.0
99	"	"	0.9489 " 19.0	17.9	101.0	117.0
101	"	"	0.7825 " 19.0	50.5	17.0	18.0
187	0.8263 " 15.0	40.6	less than 10.0	less than 10.0
			0.9670 " 15.5	15.0	91.0	105.0

The asphalt residue is of excellent quality and finds a ready sale. In fact, in some cases, the oil was used for the asphaltum only, the distillates being rejected.

The future of the oil industry appears to be bright. The southern part of the state appears to contain a large supply of petroleum, particularly in the upper part of the San Joaquin valley. There is a large demand for fuel purposes alone, and there is little doubt but that uses for the distillates will be found. Benzene derivatives appear to be present in considerable quantities and it will pay to separate them. The greatest significance, however, will be the solution of the fuel problem.

As very little has been published in regard to the character of California oils, the following results may be of value. They have been compiled from analyses made in this laboratory during the past two years. They cover oils from the various districts, and serve to show the great variance in physical characteristics.

SPECIFIC VISCOSITIES OF CRUDE OILS AT 60° F. AND 185° F. = 15½° C.
AND 85° C.

Sample number.	15½° C. 60° F.	85° C. 185° F.	Sample number.	60° F.	185° F.
145	4.88	1.28	135	282.03	3.57
134	63.15	2.12	149	1462.83	8.35
157	299.59	4.70	160	11.19	1.54
161	1.57	1.05	95	3.00	1.15
101	1759.13	7.51	99	1.17	0.96
156	373.11	3.67	100	10.35	1.34
184	10.96	1.50	186	34.28	1.84
101	1.10	0.95	192	3259.27	9.00
112	274.35	3.35	187	347.77	3.37
2	19.40	1.60	4	16.96	1.53
138	396.72	4.28	113	142.66	2.85
189	310.56	3.38			

It will be noticed that the viscosity diminishes very rapidly as the temperature increases. At a temperature of 100° the viscosity approaches that of water or may even be less.

The following table shows the percentage of volatile matter at various temperatures. It is of value chiefly as showing the variant character of the oils from different districts. The analyses were carried out under practically the same conditions, and the results are comparative.

FRACTIONAL DISTILLATION OF CALIFORNIA PETROLEUM.

Serial number. ¹	District.	Water.	Below 100° C. " 212° F.	100° C. to 150° C. 212° F. to 302° F.	150° C. to 250° C. 302° F. to 482° F.	250° C. to 350° C. 482° F. to 662° F.	350° C. to asphalt. 662° F. to asphalt.	Asphalt.	Loss.
111	Kern.	1.4	0.00	0.00	3.9	34.0	27.2	31.6	1.9
112	Kern.	0.5	0.00	1.00	9.25	19.74	48.13	21.25	..
160	Coalinga.	0.00	0.00	1.10	21.70	40.70	21.50	14.60	0.4
99	Coalinga.	0.00	0.00	32.60	28.20	17.20	16.00	5.00	1.0
51	Coalinga.	1.00	0.00	0.80	15.00	42.50	14.50	25.40	0.8
52	Coalinga.	0.20	7.70	10.30	18.70	30.00	18.00	16.20	0.9
134	McKittrick.	0.00	0.00	0.00	19.10	20.80	45.82	14.25	..
135	McKittrick.	0.00	0.00	trace	8.50	23.50	53.25	15.00	..
85	Sunset.	0.00	0.00	6.50	17.26	17.25	47.98	11.00	..
103	Sunset.	0.00	0.00	0.00	11.90	26.40	37.80	23.90	..
87	Ventura.	2.74
155	Ventura.	9.50	0.00	0.00	11.20	34.05	8.75	36.50	..
50	Ventura.	0.00	0.00	17.00	11.50	9.00	21.50	41.00	..
186	Ventura.	0.00	2.50	9.50	16.00	54.50	2.20	13.80	1.5
101	Humboldt.	0.00	0.00	39.50	29.80	24.00	1.50	4.70	0.5
161	Humboldt.	0.00	0.00	0.00	47.50	35.20	9.60	7.50	0.2
94	Humboldt.	0.00	0.00	13.70	33.40	22.20	10.80	19.40	0.5
95	Humboldt.	0.00	0.00	0.00	15.70	35.10	44.30	4.90	..
96	Humboldt.	0.00	0.00	0.00	16.10	53.60	3.20	26.50	0.5
99	Humboldt.	0.00	5.20	27.40	28.20	17.20	16.00	5.00	1.0
100	Napa.	0.00	0.00	0.00	0.00	87.00	4.20	9.00	..
96	Napa.	0.00	0.00	0.00	0.00	15.70	72.60	11.40	0.3
154	Colusa.	0.00	0.00	0.00	8.80	96.00	21.60	0.50	0.1
93	Newhall	0.00	12.50	46.20	32.27	3.23	5.30	0.5
159	Santa Clara.	0.00	15.00	35.80	31.20	14.40	3.60	..
142	Contra Costa.	5.70	0.00	3.70	17.50	37.00	15.20	21.00	0.1
127	Santa Cruz.	21.50	0.00	0.00	6.20	34.00	14.40	22.80	1.1
149	Summerland.	25.00	0.00	0.00	6.50	17.10	27.50	22.50	1.4
184	San Mateo.	14.90	0.00	0.00	0.00	0.00	58.90	26.00	0.2

The percentage of carbon and hydrogen is shown in the following table: The difference is not put down as oxygen for the reason that most of the oils contain at times considerable quantities of nitrogen and sulphur.

Oil Serial No.	Hydrogen. Per cent.	Carbon. Per cent.	Specific gravity.	District.
145	10.84	88.26	0.9700	Colusa.
114	11.30	85.80	Bakersfield.
115	11.50	86.09	0.9397	Whittier.
155	10.81	80.42	0.9830	Ojai Valley.
170	12.16	84.86	0.9572	Kern.

¹ Numbers are volume per cent.

Oil. Serial No.	Hydrogen. Per cent.	Carbon. Per cent.	Specific gravity.	District.
156	10.72	86.32	0.9572	Bakersfield.
110	11.18	82.45	0.9760	Kern.
134	11.45	86.06	0.9458	McKittrick.
157	11.30	85.75	0.9533	Kern.
103	11.30	85.83	0.9589	Sunset.
142	10.83	84.66	0.9653	Contra Costa.
177	10.70	84.74
169	11.80	87.62	0.8620	Coalinga.
162	12.10	87.41
...	12.74	86.99	0.8059
...	11.82	86.61
100	11.13	88.08	0.9603	Napa County.
161	12.03	86.69	0.8810	Humboldt.
159	12.88	86.08	0.8515	Santa Clara.

The percentage of sulphur and nitrogen is shown in the following table: Various methods were tried for the determination of the sulphur, but the most accurate and convenient was to effect the combustion of the oil in oxygen at twenty-five atmospheres pressure in a Mahler bomb, and determine the sulphuric acid produced. Apparently none of the sulphur escaped oxidation. On allowing the gases to pass through bromine water, the solution gave no trace of sulphuric acid.

The Kjeldahl method was used for determining the nitrogen. Oxidation was slow but complete.

SULPHUR AND NITROGEN IN CALIFORNIA PETROLEUMS.

Number.	Specific gravity.	Nitrogen. Per cent.
1	0.8254	0.001
103	0.9589	0.047
115	0.9306	0.669
169	0.8679	0.100
171	0.9774	0.0278
172	0.9629	0.185
174	0.8749	0.243
175	0.8801	0.204
150	0.9720	0.155
		Sulphur. Per cent.
154	0.8229	0.50
156	0.9572	0.80
157	0.9533	0.668
159	0.8515	0.920
169	0.8679	0.062
135	0.9628	0.880
134	0.9458	0.870
115	0.9397	0.700
112	0.9651	0.950
103	0.9589	0.86

The following table shows the calorific value of various California oils. The determinations were made in a Mahler bomb, with oxygen at 25 atmospheres pressure, in the usual manner.

CALORIFIC VALUE OF CALIFORNIA PETROLEUMS.

Number.	Specific gravity.	°Bé.	Calorific value.	
			T. U. (calories.)	B. T. U.
103	0.9589	16.3	10,380	18,684
111	0.9760	13.5	10,190	18,342
112	0.9651	15.2	10,471	18,847.8
113	0.9518	17.5	10,350	18,630
115	0.9397	19.5	10,827	19,488.6
129	0.8861	28.6	10,800	19,440
134	0.9458	18.5	10,375	18,675
135	0.9628	15.6	10,317	18,570.6
...	0.9276	21.1	10,531	18,956
159	0.8515	34.4	11,192	20,145.6
145	0.9700	14.5	10,360	18,648
115	0.9397	19.3	10,725	19,305
156	0.9572	16.5	10,359	18,646.2
110	0.9760	13.5	10,263	18,473.4
157	0.9533	17.2	10,443	18,797.4
103	0.9589	18.0	10,380	18,684

Many more results of determinations might be given, but the foregoing serve to give an idea of some of the characteristics of California crude petroleum, and indicate the great diversity in physical properties. Chemically, they resemble each other much more closely, as will be shown in a subsequent paper.

CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA,
BERKELEY, CALIFORNIA, JANUARY 9, 1903.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 83].

THE INFLUENCE OF ATMOSPHERIC OXIDATION UPON THE COMPOSITION AND ANALYTICAL CON- STANTS OF FATTY OILS.

BY H. C. SHERMAN AND M. J. FALK.

Received May 6, 1903.

It is well known that the so-called non-drying and semi-drying as well as the drying oils may absorb oxygen from the air at ordinary temperatures and that the analytical constants are more or less changed by such oxidation. This subject was studied by Ballantyne¹ who found that olive, rape, cottonseed, arachis and linseed oils after exposure to sunlight in uncorked bottles showed

¹ *J. Soc. Chem. Ind.*, 10, 29 (1891).

lower iodine figures, higher specific gravities and higher temperature reactions with sulphuric acid. These changes took place without alteration of the volume of the oil and independently of the appearance of rancidity or free acid. In fact, there was no increase in acidity in olive, rape and arachis and only a very slight increase in the cottonseed and linseed oils.

Having found that such oxidation is less dependent upon sunlight and occurs more often in stored samples than is commonly supposed, we undertook a comparison of the changes produced in some of the constants to ascertain whether any quantitative relations could be traced which would enable one to judge the original nature of the oil from the results obtained upon a sample thus altered by exposure.

Samples of oils of about 200 grams each were allowed to stand for several months, with occasional shaking, in uncorked bottles, loosely covered to exclude dust, on a shelf in the laboratory which was frequently exposed to direct sunlight. No special effort was made to give the different samples the same amount of exposure and shaking since it seems impossible to control all the conditions which affect the rate of oxidation. These "exposed" samples were then compared with duplicate samples from the same packages which had been kept in well-filled, air-tight bottles or cans in a dark closet. Many of the oils had been analyzed when first received and in all such cases the agreement between the results first obtained and those found on the carefully protected samples was sufficiently close to show that no appreciable change had taken place in the latter.

The table which follows shows the changes which had taken place in the samples exposed to the air.

In each case there is a decrease in the Hübl figure (percentage of iodine absorbed) and an increase in specific gravity and temperature reaction with sulphuric acid. There is also, in each case, a slight increase in acidity and in the proportion of volatile acids present, but these changes are irregular and much too small to account for the changes in the other figures. These results show that the rise in temperature with sulphuric acid is not necessarily parallel with the Hübl figure and should not be used instead of the latter, but rather in connection with it. For instance, a sample of pure olive oil which had taken up oxygen from the air would, if judged by the high specific gravity and high temperature reaction.

be condemned as adulterated, whereas these results considered in connection with the low Hübl figure would at once indicate the true nature of the sample.

CHANGES PRODUCED IN ANALYTICAL "CONSTANTS" BY EXPOSURE TO
LIGHT AND AIR.

Description of oil.	Specific gravity 15.5 15.5	Temp. reaction.			Free acid as oleic.	Reichert- Meissl figure.
		Hübl figure. ¹	Maumené. ²	Mitchell. ³		
Olive oil (2058) fresh.....	0.917	83.8	100	16.9	2.65	0.43
" " " after exposure.....	0.923	77.4	127	20.3	3.27	0.75
Lard oil (2057) fresh.....	0.917	73.3	106	16.7	0.90	0.56
" " " after exposure.....	0.927	66.7	116	18.4	1.92	1.59
Cottonseed oil (2053) fresh.....	0.920	102.8	161	21.4	0.14	0.16
" " " after exposure....	0.934	92.0	215	27.0	1.27	1.96
Cottonseed oil (2055) fresh.....	0.923	105.2	171	20.3	0.07	...
" " " after exposure....	0.937	92.9	217	27.2	1.29	...
Maize oil (2056) fresh.....	0.924	117.2	174	...	2.78	0.60
" " " after exposure.....	0.935	107.0	216	...	4.59	1.40
Poppyseed oil (2069) fresh.....	0.923	125.3	202	25.2	2.75	...
" " " after exposure....	0.931	117.1	214	27.7	3.63	...
Seal oil (2103) fresh.....	0.926	145.3	0.69	1.00
" " " after exposure.....	0.947	120.3	3.39	2.40
Linseed oil (2070) fresh.....	0.938	177.1	...	30.5	1.26	...
" " " after exposure.....	0.954	148.1	...	34.3	2.05	...
Linseed oil (2052) fresh.....	0.934	178.0	...	31.3	1.33	0.49
" " " exposed 4 months ..	0.942	165.8	2.23	1.10
" " " " 8 " ...	0.966	139.4	...	32.8	4.45	2.64

In the case of the linseed oil (No. 2025), where the greatest amount of oxidation had taken place, it seemed desirable to determine the effect upon the elementary composition to find if possible whether oxygen or hydroxyl had been added. In addition to the unchanged oil and the portion which had been exposed in a bottle for eight months, another portion which had been exposed in a thin layer until semi-solid was analyzed. The results were as follows:

¹ Determinations of the Hübl figure were carried out as previously described (this Journal, 23, 168), using only the purest obtainable reagents and allowing always an excess of iodine about equal to the amount absorbed.

² Specific temperature reaction (referred to that of water as 100) on mixing 10 cc. of concentrated sulphuric acid with 50 grams of the sample.

³ The figures in this column show the actual rise of temperature (in degrees centigrade) on mixing 10 cc. of concentrated sulphuric acid with a solution of 10 grams of the sample in 50 cc. of carbon tetrachloride.

	Carbon.	Hydrogen.	Oxygen.	Ratio C:H.
Linseed oil, unchanged.....	75.46	10.92	13.62	1:0.145
" exposed eight months..	73.23	10.46	16.31	1:0.143
" " till semi-solid..	69.03	10.06	20.91	1:0.146

In this case, therefore, the net result of the exposure was an increase in oxygen without any appreciable change in the ratio of carbon to hydrogen. This is practically in agreement with the experience of Bauer and Hazura in an experiment¹ in which a thin film of linseed oil was allowed to dry quite completely in the air.

It has already been shown² that atmospheric oxidation decreases the heat of combustion of fatty oils to an extent nearly proportional to, but slightly greater than, the increase in the specific gravity. This relation may now be explained somewhat more fully. The linseed oil (No. 2052) on exposure in bulk for eight months increased in specific gravity from 0.934 to 0.966 or 3.43 per cent., calculated on the original weight. The analyses show that it took up oxygen to the extent of 3.16 per cent. of its original weight. The greater increase in specific gravity is probably due to a slight contraction in volume. The original heat of combustion was 9364 calories per gram. Correcting for the increase in weight we have $9364 \div 1.0343 = 9053$ calories, but since the sample took up 3.16 per cent. of its weight of oxygen the "available hydrogen" must have been diminished by 0.395 per cent. of the original or 0.38 per cent. of the increased weight, requiring a further reduction of 131 calories. This gives an estimated heat of combustion for the exposed sample of 8922 calories per gram. Taking the increase in specific gravity as a direct measure of the oxygen absorbed, this calculated value would be 8910 calories. The value as determined by combustion in the bomb-calorimeter was 8899 calories per gram. These figures agree within the limits of experimental error and confirm the suggestion made in a previous paper that the heat of combustion taken in connection with the specific gravity may prove a useful factor in the study of the fatty oils.

With glycerides other than those having strong drying properties, it may be considered as practically established by the work of Hazura that the oxidation consists essentially in the addition of hydroxyl to the unsaturated fatty acids, oleic being converted into dioxystearic, and linolic into sativic acid. If, as stated by Ballan-

¹ *Monatsh. Chem.*, 9, 459 (1888).

² This Journal, 23, 164: 24, 348.

tyne,¹ the oxidation takes place without change in volume, the increase in specific gravity due to the introduction of hydroxyl should be directly proportional to the decrease in iodine-absorbing power due to the saturation of the double bonds. The quantitative relation would then be:

Percentage increase in specific gravity:Decrease in Hübl figure::OH:I, or as 17.008:126.85, or as 1:7.46.

Thus the sample of olive oil shown in the table above had increased in density from 0.917 to 0.923 or 0.65 per cent. The Hübl figure of the exposed sample was 77.4. Adding to this $7.46 \times 0.65 = 4.9$, we obtain as a corrected value 83.3 as against 83.8, the Hübl figure of the unchanged sample.

Correcting, according to the same proportion, the Hübl figures of all the "exposed" oils in the table we obtain the "recalculated" values given in Column III.

Sample.	Hübl figure.		
	I. In fresh condition.	II. After ex- posure.	III. Recalcu- lated.
Olive oil (2058).....	83.8	77.4	83.3
Lard oil (2057).....	73.3	66.7	74.8
Cottonseed oil (2053).....	102.8	92.0	103.3
Cottonseed oil (2055).....	105.2	92.9	104.2
Maize oil (2056).....	117.2	107.0	115.9
Poppyseed oil (2069).....	125.3	117.1	123.6
Seal oil (2103).....	145.3	120.3	137.2
Linseed oil (2070).....	177.1	148.1	161.0
Linseed oil (2052) after 4 months...	178.0	165.8	172.2
" (2052) " 8 " ...	178.0	139.4	165.0

In the first five samples, representing non-drying and semi-drying oils, the difference between the original and the recalculated Hübl figure is in no case greater than 1.5, while the difference for the average of the five samples is only 0.2 per cent. Poppyseed oil which is usually classed as a drying oil, but which is also edible, shows a discrepancy of 1.7 per cent. It appears, then, that with such oils the results obtained on an exposed sample may be recalculated according to the proportion above given, if either the original specific gravity or the original Hübl figure is known.

When neither of these is known, assume as the original specific gravity the average figure for the variety of oil under examination, calculate the apparent increase in specific gravity (in percentage of the original) and then recalculate the Hübl figure as above. If

¹ *Loc. cit.*

the oil is unadulterated, the recalculated Hübl figure should be within the limits of variation of pure fresh samples.

This method cannot be relied upon for oils containing the more highly unsaturated acids (drying oils, fish oils, etc.), since in such oils there is, as shown by analysis, either a direct absorption of oxygen as such or a condensation with elimination of water from the hydroxyl groups first added, probably accompanied by a slight contraction in volume.

As regards the examination of edible oils, however, the results here given may be said (1) to emphasize the importance of determining both the Hübl figure and the specific gravity, whatever other determinations are made, and (2) to show how the mutual relations of these constants enable one to interpret the results obtained upon samples greatly altered by exposure to atmospheric oxidation.

NEW YORK CITY,
May 1, 1903.

COMPOSITION OF THE "BREAK" FROM LINSEED OIL.¹

BY GUSTAVE W. THOMPSON.

Received May 15, 1903.

FRESHLY pressed linseed oil, or linseed oil that has not been properly settled or prepared for the manufacture of varnish, when heated to, say, 400° Fahrenheit, undergoes a change which the varnish man describes as "breaking". The phenomenon consists in the appearance in the oil of gelatinous masses slightly darker than the oil itself, settling with difficulty and extremely difficult to remove from the oil by filtration. The bulk of the break appears in some instances to be very considerable. The following experiments, however, will show that the percentage, by weight, present is very small.

Twenty-five hundred grams of linseed oil were heated to the breaking-point. The oil was allowed to cool and then filtered. The precipitate clogged the filter considerably, which necessitated its removal to a glass vessel, in which it was washed with petroleum ether, by decantation. Finally, a non-oleaginous residue was obtained, weighing 6.93 grams, equal to 0.277 per cent. of the original oil. On ignition, a portion of this residue was shown to

¹ Read before the New York Section of the American Chemical Society, May 8, 1903.

COMPOSITION OF THE "BREAK" FROM LINSEED OIL. 717

contain 47.79 per cent. ash—equal to 0.1177 per cent. of the original oil. The oil, which was filtered from the break, was shown to contain 0.0039 per cent. ash. The following is an analysis of the ash from the break :

CaO	20.96
MgO	18.54
P ₂ O ₅	59.85
SO ₃	trace
	<hr/>
	99.35

The first thing to note is that the phosphoric anhydride is present in the ash from the break in excess of what would form an orthophosphate when combined with the bases present. It appears, in fact, that the oxygen present in the phosphoric anhydride is to the oxygen in the bases in the ratio of 5 to 2, corresponding closely with that required by a pyrophosphate. The composition of the organic matter in this sample of break was not determined.

Ash determinations were made on a number of samples of oil, the following being a few of the results:

	Ash. Per cent.
No. 1, Fresh double-filtered raw American linseed oil	0.1429
No. 2, " " " " " " " "	0.1967
No. 3, Good, well-settled " " " "	0.0609
No. 4, Best American linseed varnish oil.....	trace

The ash from sample No. 1 was analyzed, with the following results:

	Per cent. of the oil.
CaO	0.0235
MgO	0.0221
P ₂ O ₅	0.0705
K ₂ O	0.0043
SO ₃	0.0227
	<hr/>
	0.1431

It should be noted that here, also, the phosphoric acid, is in excess of the bases, and is present largely in the pyro form.

Mulder speaks of the presence of calcium sulphate in linseed oil, but, so far as we know, no mention has been made of the presence of phosphates.

In order to locate the origin of the constituents of the linseed oil ash, analyses were made of the ash from American flaxseed, and flaxseed cake made therefrom, which analyses are given here:

	Flaxseed. Per cent.	Oil cake. Per cent.
Ash.....	3.112	4.899
Composition of ash.		
SiO ₂	1.83	1.51
Fe ₂ O ₃ + Al ₂ O ₃	1.25	1.59
CaO	0.46	9.24
MgO.....	18.31	18.52
K ₂ O	26.18	26.14
Na ₂ O	1.71	3.59
SO ₃	3.96	3.51
P ₂ O ₅	35.44	36.28
	98.14.	100.38

These analyses confirm, in the main, analyses already published. If we consider the ratio between the oxygen in the bases and the oxygen in the phosphoric anhydride in an orthophosphate to be as 3 is to 5 we find here that the bases are in excess. It is worthy of notice here that the phosphoric acid, lime and magnesia are dissolved, to some extent, by the oil, while the potash, which is the principal base, is taken up by the oil, only to a very slight extent.

In examining the mucilage from various plants, Schmidt and Kirchner, and Tollens¹ reported the presence of phosphates in the mucilage which they separated from the flaxseed; it seems probable that these phosphates in the seed are largely combined with the mucilage, and that the mucilage and the phosphates combined therewith are dissolved, to some extent, by the oil. This conclusion, however, requires confirmation. Examining a portion of thoroughly extracted break for mucilage, we obtained no reaction. The test made was to heat the break with dilute hydrochloric acid for a few seconds, filter and add alcohol. No precipitate was obtained. It may have been that the mucilage was decomposed at the temperature to which it was subjected. We have not been able, as yet, to pursue our inquiries further along this line.

As to the presence of albuminoids in linseed oil, our experiments have been as follows: The determination of nitrogen in a sample of linseed oil showed less than 0.01 per cent. The same sample of oil showed 0.04 per cent. of phosphorus. This would indicate that, relatively speaking, the phosphates present were considerably greater than the nitrogenous matter. An examination, for nitrogen, of a portion of extracted break indicated that some was present although the amount was less than 1 per cent. of the break. The phosphorus, on the other hand, amounted to 9.60 per

¹ *Ann. Chem. (Liebig)*, 51, 175 and 215.

cent. of the break. This, figured to P_2O_5 , amounted to 57 per cent. of the ash in the break. It would seem unjustifiable to calculate the phosphorus present in the linseed oil to lecithin, on account of the large percentage of bases present. Inasmuch as albuminoids coagulate at a low temperature as compared with the breaking temperature of linseed oil, we feel that any assumption that albuminoids are present is unjustified. We do, however, feel justified in saying that the principal cause of the break in linseed oil is the phosphates of lime and magnesia present, although their presence in the oil may be due to a combination between them and some organic base or bases.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON A CLASS OF PSEUDOTHIUREAS DESCRIBED AS NORMAL UREAS.

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

Received April 22, 1903.

WHEN thioamides are treated with alkyl halides, compounds are formed having the alkyl group attached to sulphur. In the normal thioureas, for example, it is the sulphur and not the nitrogen that is the point of attack. When a radical is attached to sulphur then further alkylation may take place on the nitrogen.¹ At least this has been found to be true in all cases that have been thoroughly examined.

There are some thioureas, however, that have been represented as yielding nitrogen alkyl derivatives with halides. Wunderlich² found that sodium cyanamide unites with mustard oils in alcoholic solution, giving the sodium salts of alkylcyanthiureas $RNHCSNH_2CN$, and by treating these salts with alkyl halides the sodium was shown to be replaced by alkyls. The resulting dialkyl compounds were represented by the general formula $RNH-CSNR'CN$.

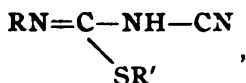
Later, Hecht³ prepared a large number of these compounds. He represents them by the formula above, but he remarks that further work will be necessary to determine their structure and he states that this will be the subject of a later paper. Thirteen years

¹ Bertram : *Ber. d. chem. Ges.*, 25, 48 (1892).

² *Ber. d. chem. Ges.*, 19, 448 (1886).

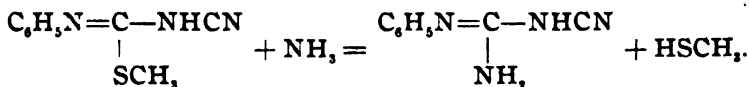
³ *Ber. d. chem. Ges.*, 23, 1658 (1890).

have now passed and these compounds have not been further examined. From what has just been said, it seemed doubtful that the entering alkyl group attaches itself to nitrogen. We therefore undertook the determination of the structure of these ureas, and we will now show that they are incorrectly represented in the literature—that they are pseudothioureas and not derivatives of normal thioureas. Their structure is to be represented by the general formula.

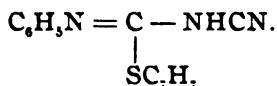


in which R' is the alkyl of the alkyl halide.

Sodium cyanamide was treated in alcoholic solution with phenyl mustard oil. The crystalline salt thus obtained was heated with methyl iodide according to the directions of Hecht. The pure product melted, as he states, at 186°. When this was suspended in strong alcoholic ammonia, a reaction slowly took place and methyl mercaptan made its presence known. In order to get a complete reaction, it was necessary to heat in a closed tube at 90°-95°. The crystalline product was then free from sulphur and, on analysis, gave results agreeing with those calculated for phenylcyanoguanidine. The reaction took place as follows:



In addition to the above phenylcyanthiolmethylpseudothiourea, we have prepared and examined phenylcyanthiolbenzylpseudothiourea, the phenylthiocarbaminbenzylcyanamide of Hecht. This compound has the structure

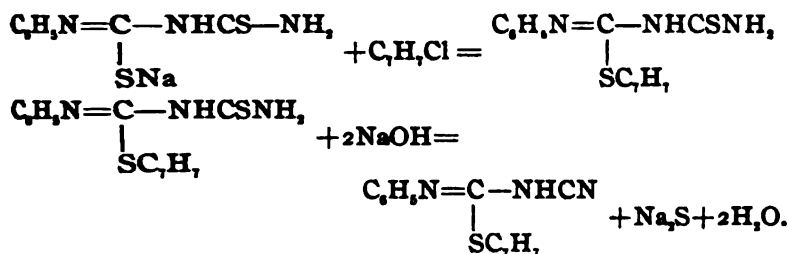


We find also that it is identical with Fromm's phenyl- ψ -benzyl-sulphoharnstoffcyanide, a fact which apparently escaped the notice of Professor Fromm.¹ He gives the melting-point at 190°. Hecht states that the substance melts at 182°. We have prepared the compound by both methods and both preparations melted at 182°-183°. When mixed, the melting-point was not altered. We have also prepared the corresponding methyl deriva-

¹ *Ber. d. chem. Ges.*, 28, 1304 (1895).

tive by both methods and find that these products are identical.

The preparation of Hecht's compounds by Fromm's method offers further proof that the compounds are pseudothiureas. This method consists in treating phenyldithiobiuret with three molecular proportions of alkyl halide and four of alkali. The reaction is represented as follows:



Fromm has shown that when the phenylcyanthiolbenzylpseudothiurea is boiled with hydrochloric acid it takes up the elements of water and separates aniline, forming thiolbenzylallophanic ester, $\text{C}_7\text{H}_7\text{S}.\text{OC}-\text{NHCONH}_2$. This shows that the alkyl group is attached to sulphur.

The pseudothiureas containing a $-\text{CN}$ group are more stable and less reactive than other pseudothiureas. They have acid properties and form salts even with ammonia.

It was found that phenylcyanthiolbenzylpseudothiurea could be crystallized unaltered from boiling acetic anhydride. Benzoyl chloride failed to react with the compound in the Schotten-Baumann process, and little or no mercaptan was given off on heating on the steam-bath or at 150° with aniline or with phenylhydrazine. These compounds, therefore, depart widely in properties from other classes of pseudothiureas.

Phenylcyanguanidine, $\text{C}_6\text{H}_5\text{N}=\text{C}(-\text{NH}_2)-\text{NHCN}$.—Phenylcyanthiolmethylpseudothiurea was heated with an excess of alcoholic ammonia at 90° - 95° for five hours. Mercaptan escaped, on opening the tube, and from the alcoholic solution bunches of colorless needles were obtained. These were moderately soluble in warm alcohol and could be crystallized from water. The substance dissolved in warm alkali and was precipitated by mineral acids. It melted at 190° - 191° without decomposition, and a nitrogen determination gave:

	Calculated for $\text{C}_6\text{H}_5\text{N}_4$	Pound.
Nitrogen	35.0	35.2

The *ammonium salt* of phenylcyanthiolumethylpseudothiourea was obtained when the pseudothiourea was heated at 100° for five hours with alcoholic ammonia saturated with hydrogen sulphide. On cooling, no pressure was found in the tube and, on concentrating the solution, colorless needles separated which, after two recrystallizations, melted at about 142°-143° to a pale yellow liquid. A nitrogen determination gave:

	Calculated for	Found.
	$C_6H_5N=C(-SCH_3)-NHCN.NH_4C_6H_{12}N_4S.$	
Nitrogen.....	26.82	26.79

NEW HAVEN, CONN., April 17, 1903.

THE BASIC OXALATES OF BISMUTH.

BY F. B. ALLAN.

Received May 20, 1903.

IN recent papers the author has given the results of researches on the nitrates¹ and sulphates² of bismuth, making use of the phase rule to determine the number of phases present, and thus to know whether the solid to be analyzed was one phase or a mixture of two phases. In a monovariant system of three components, we may have a gaseous, a liquid, and two solid phases. In a divariant system, only three phases can exist and there can be only one solid in addition to the liquid and gaseous phases, and it is only in the latter case that we can call the solid a chemical compound. In the experiments referred to, both monovariant and divariant systems were obtained, but as three weeks were sometimes necessary to obtain equilibrium in a monovariant system, no attempt has been made to get other than divariant systems in this research.

Heintz³ added oxalic acid to a solution of bismuth oxide in nitric acid, and boiled the precipitate repeatedly with water. He supposed that the neutral oxalate is first formed, and that it is decomposed by water; he gives the resulting substance the formula $Bi_2O_3 \cdot 2C_2O_3 \cdot 1\frac{1}{2}H_2O$. Schwartzberg⁴ boiled bismuth oxide with acid potassium oxalate, and the product dried at 100° agreed with the formula $Bi_2O_3 \cdot 3C_2O_3 \cdot 4H_2O$. Souchay and Lensson⁵ prepared the neutral oxalate and gave the composition of the air-dried salt

¹ *Am. Chem. J.*, 28, 307.

² *Ibid.*, 27, 284.

³ *Pogg. Ann.*, 63, 90.

⁴ *Ann. Chem. (Liebig)*, 64, 127.

⁵ *Ibid.*, 108, 245.

TABLE A.
 $\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in $\text{Bi}_2\text{O}_3\text{C}_2\text{O}_3 = 2.15$.
 Temp. 50° . $\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in $\text{Bi}_2\text{O}_3\text{C}_2\text{O}_3 = 3.23$.

Components.		Time.	Composition of solution.	$\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in solid.
	100 cc. water.			
1 gram neutral oxalate.	100 "	3 days	0.0225 N. oxalic acid.	3.33
2 grams "	100 "	3 "	0.0435 "	3.27
3 " "	100 "	3 "	0.0647 "	3.26
4 " "	100 "	3 "	0.0857 "	3.25
2 " "	100 cc. 0.042 N. oxalic acid.	7 "	0.085 "	3.25
2 " "	100 " 0.019 "	3 "	0.069 "	2.21
2 " "	100 " 0.14 "	3 "	0.138 "	2.15
2 " "	100 " 0.21 "	3 "	0.205 "	2.16
2 " "	100 " 0.34 "	3 "	0.34 "	2.12
2 " "	100 " 0.70 "	3 "	0.68 "	2.12

as $\text{Bi}_2\text{O}_3 \cdot 3\text{C}_2\text{O}_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$, while Muir¹ gave it the formula $\text{Bi}_2\text{O}_3 \cdot 3\text{C}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. I could not obtain this salt free from the basic oxalate although it was stirred for several days with a concentrated oxalic acid solution. Souchay and Lensson boiled the neutral oxalate repeatedly with water and obtained the basic salt $\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and Muir repeating this preparation gave it the formula $\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3$.

In the following experiments, the neutral oxalate, containing some basic oxalate, was stirred with water or oxalic acid solutions, the apparatus used being the same as that previously described. The composition of the solid contents was determined by the analysis of the liquid phase.

TABLE B.
Temp. 75°.

Components.		Time.	Composition of solution.	$\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in solid
1 gram neutral oxalate	100 cc. water	3 days	0.024 N. oxalic acid	3.35
2 grams " "	100 " "	3 "	0.046 " "	3.27
3 " " "	100 " "	3 "	0.068 " "	3.28
4 " " "	100 " "	3 "	0.090 " "	3.26
5 " " "	100 " "	3 "	0.122 " "	3.21
6 " " "	100 " "	3 "	0.135 " "	3.25

At 50° the basic salt is in equilibrium with oxalic acid solutions up to 0.085 normal, and at 75° up to at least 0.135 normal. In the sixth experiment in Table A the reaction is delayed by the initial strength of the oxalic acid solution. The basic salt obtained in these experiments was air-dried and dissolved in hydrochloric acid. The bismuth was determined as the sulphide and the oxalic acid in the filtrate was titrated directly with permanganate, as the small quantity of hydrochloric acid present did not effect the result.

	Calculated for $\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3 \cdot \text{H}_2\text{O}$.	Found.
Bi_2O_3	74.16	74.14
C_2O_3	22.97	23.00
H_2O	2.87	(2.86)

Miller and Kenrick² have shown that the number of possible phases is not changed if a new constituent be added to the liquid phase, provided that this new constituent does not pass into the solid phase. This condition is fulfilled, if dilute ammonia is stirred with $\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and therefore a divariant system

¹ *J. Chem. Soc. (London)*, 1878, p. 193.

² *Trans. Roy. Soc., Canada*, 1901.

TABLE C.
Temp. 75°.

Components.				Time.	$\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in solid.
1 gram $\text{Bi}_2\text{O}_3 \cdot \text{C}_2\text{O}_3 \cdot \text{H}_2\text{O}$,	100 cc. 18	per cent. NH_4NO_3 ,	and 0.0275 N. NH_3		
1 "	100 "	18 "	" 0.0457 "	1 day	3.55
1 "	100 "	18 "	" 0.011 "	1 "	3.84
1 "	100 "	18 "	" 0.011 "	1 "	5.28
1 "	100 "	3.6 "	$(\text{NH}_4)_2\text{C}_2\text{O}_4$ " 0.0275 "	1 "	3.20
1 "	100 "	3.6 "	" " " 0.0457 "	1 "	3.20
1 "	100 "	3.6 "	" " " 0.091 "	1 "	3.20

TABLE D.

Temp. 75°. $\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in $3\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3 = 9.69$.

Components.		Time.	Composition of solution. 0.0703 N. oxalate (neutral).	$\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in solid.
1 gram $\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3 \cdot \text{H}_2\text{O}$.	100 cc. 0.028 N $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and 0.0462 N. NH_3 .			
1 "	100 " 0.028 "	2 days	0.0703	8.82
1 "	100 " 0.028 "	2 "	0.0720	9.70
1 "	100 " 0.028 "	2 "	0.0720	9.70
1 "	100 " 0.028 "	2 "	0.0720	9.70
1 "	100 " 0.028 "	2 "	0.0724	9.79
1 "	100 " 0.028 "	2 "	0.0731	9.90
1 "	100 " 0.028 "	2 "	0.0720	9.70
1 "	100 " 0.028 "	2 "	0.0743	10.50

still contains but one solid phase. In the following experiments, ammonia of varying strength was used and another basic salt was obtained. Preliminary experiments showed that the new basic salt was acted upon by quite dilute ammonia, and in order to obtain this solid phase in equilibrium with a larger range of concentrations of ammonia, it was necessary to reduce the efficiency of the ammonia in the reaction. This can be done by adding to the solution any ammonium salt, thus decreasing the amount of ionization, and as ammonium oxalate is one of the products of the reaction, it is the best salt for this purpose. Table C contains a comparison of the rate of reaction in the presence of ammonium nitrate and of ammonium oxalate, and shows that although the ammonium oxalate was more dilute, the reaction was much quicker in the ammonium nitrate solution.

Nos. 2 to 7 in Table D are divariant systems with one solid phase. The solid contents of these bottles were filtered off, air-dried, and analyzed.

	Calculated for $3\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_4$	Found.
Bi_2O_3	90.64	90.42
C_2O_4	9.36	9.47

This basic salt has not been previously described.

TABLE E.
Temp. 50° .

Components.		Time.	$\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_4}$ in solid.
1 gram $\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_4$	100 cc. 0.093 N. NH_3	4 days	1.16
1 " "	100 " 0.465 "	4 "	2.21
1 " "	100 " 0.07 N. KOH	4 "	6.63
1 " "	100 " 0.10 "	4 "	Bi_2O_3 .

Table E shows the results obtained when the higher basic oxalate reacts with more concentrated ammonia, or with potassium hydroxide. There is no indication of another basic salt.

Neutral bismuth oxalate was stirred with solutions of potassium oxalate and of ammonium oxalate, but the reaction was found to be slow, and it was difficult to obtain equilibrium. The composition of the solids obtained indicated the existence of double salts having the formulas $\text{Bi}_2(\text{C}_2\text{O}_4)_3(\text{NH}_4)_2\text{C}_2\text{O}_4$ and $\text{Bi}_2(\text{C}_2\text{O}_4)_3\text{K}_2\text{C}_2\text{O}_4$, and Souchay and Lensson's experiments in which they found more complex double salts were repeated, and the products analyzed by Messrs. DeLury and Phillips. Their results are published in this Journal.

A NEW DOUBLE OXALATE OF BISMUTH AND POTASSIUM.

BY F. B. ALLAN AND J. S. DELURY.

Received May 20, 1903.

By dissolving bismuth oxalate in concentrated, hot potassium oxalate and cooling the solution, Souchay and Lensson¹ obtained a substance to which they gave the formula



and from the mother-liquor they got a further deposit having the composition



Svensson² has also described a double salt having the composition



When a small quantity of bismuth oxalate is stirred with a saturated potassium oxalate solution, the solid phase is found to be potassium oxalate containing only a trace of bismuth, the bismuth oxalate having displaced the potassium oxalate in the solution. If more dilute solutions of potassium oxalate be used, the solid phase approaches the composition $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot \text{K}_2\text{C}_2\text{O}_4$, but the double salt was not obtained pure in this way.

Bismuth oxalate was boiled with a 20 per cent. solution of potassium oxalate; the hot solution was filtered and, on cooling, deposited small, white crystals. These crystals, dried under pressure, were dissolved in hydrochloric acid and the solution, after the removal of bismuth, was evaporated to dryness, ignited, and the potassium determined as potassium chloride; the bismuth was determined as the sulphide and the oxalic acid by titration with permanganate.

	Calculated for $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 11\text{K}_2\text{C}_2\text{O}_4 \cdot 9\frac{1}{2}\text{H}_2\text{O}.$	Found.
Bismuth	40.94	40.91
C_2O_4	34.56	34.54
Potassium	7.69	7.69
Water	16.81	(16.86)

A 21 per cent. and a 23 per cent. solution of potassium oxalate gave the same double salt. Bismuth oxalate was then boiled with a solution of potassium oxalate saturated at room temperature and the deposit at 50° contained 36.1 per cent. C_2O_4 while that ob-

¹ *Ann. Chem. (Liebig)*, 108, 245.

² *Ber. d. chem. Ges.*, 3, 314.

tained by cooling the same solution from 50° to room temperature contained 51.9 per cent. C_2O_4 . As the oxalates described by Souchay and Lensson would contain 41.9 per cent. and 49 per cent. C_2O_4 respectively, it seems probable that the precipitates from the more saturated solutions are mixtures of the double salt described above and potassium oxalate.

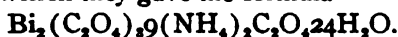
CHEMICAL LABORATORY UNIVERSITY
OF TORONTO, May, 1903.

ANew DOUBLE OXALATE OF BISMUTH AND AMMONIUM.

BY F. B. ALLAN AND T. A. PHILLIPS.

Received May 20, 1903.

SOUCHAY AND LENSSON¹ dissolved bismuth oxalate in concentrated, hot ammonium oxalate solution and obtained, on cooling, a double salt to which they gave the formula



Their analyses do not agree very closely with that formula, and as some experiments made in this laboratory threw doubt on the existence of this complex double salt, their work has been repeated.

A 4 per cent. solution of ammonium oxalate was boiled with bismuth oxalate, using a reflux condenser, for about half an hour, and filtered hot. On cooling, this solution deposited small, white crystals which were dried, under pressure, between paper. The salt was easily soluble in hydrochloric acid. The bismuth was determined as the sulphide, the oxalic acid by titration with permanganate, and the ammonia distilled over by boiling with potash. absorbed in hydrochloric acid and determined in the usual way.

	Calculated for $Bi_2(C_2O_4)_3 \cdot 9(NH_4)_2C_2O_4 \cdot 24H_2O.$	Found.
Bismuth	43.93	44.30
C_2O_4	37.08	36.85
Ammonium	3.81	3.78
Water ..	15.18	(15.07)

Bismuth oxalate is only slightly soluble in ammonium oxalate, and large quantities of the solution must be used in preparing the double salt, so that imperfect filtering or the slight solubility of basic salt formed during the boiling would account for the high value found for bismuth and the corresponding low values for oxalic acid and ammonia.

¹ *Ann. Chem.* (Liebig), 108, 245.

More of the double salt was prepared by using ammonium oxalate solution saturated at 25° . The precipitate deposited at 50° gave 3.85 per cent. of ammonia and was, therefore, the same compound as the first, but when this solution cooled to room temperature, it yielded two kinds of crystals which, under the microscope, were identified as the double salt and ammonium oxalate, and it would appear that the salt described by Souchay and Lensson was a similar mixture.

CHEMICAL LABORATORY, UNIVERSITY
OF TORONTO, May, 1903.

DOUBLE HALIDES OF TELLURIUM WITH THE ALKALOIDS.

BY VICTOR LENHER AND WINIFRED TITUS.

Received April 27, 1903.

It has been previously shown¹ that the chloride and bromide of tellurium unite with the salts of the amines to form a series of double salts in which the types of H_2TeCl_6 and H_2TeBr_6 are consistently followed. The hydrogen of these acids may be considered as having been directly replaced by the complex ammonium group, or the tellurium halide may be looked at as uniting with the molecules of the hydrochloride or hydrobromide of the amine.

Following the same line of work with the alkaloids, there appear types which differ considerably from the first or most simple type.

In some cases 1 molecule of the alkaloid unites with 1 molecule of H_2TeCl_6 or H_2TeBr_6 , while in others 2 molecules of the alkaloids unite with 1 molecule of the tellurium halogen acids. As a rule, the salts appear to follow the type of compounds that H_2PtCl_6 forms with the alkaloids, for example, with quinine there appear the salts $C_{20}H_{24}N_2O_2 \cdot H_2PtCl_6 + H_2O$ and $C_{20}H_{24}N_2O_2 \cdot H_2TeCl_6$, while with morphine $(C_{17}H_{19}NO_3)_2 \cdot H_2TeCl_6$ is analogous to $(C_{17}H_{19}NO_3)_2 \cdot H_2PtCl_6 + 6H_2O$.

However, the chloroplatinate usually crystallizes with water of crystallization while these new compounds are anhydrous.

The method of procedure for the formation of these compounds consists in adding a strong solution of tellurium dioxide in hydrochloric or hydrobromic acid to a concentrated solution of the alkaloid in the corresponding acid.

¹ This Journal, 22, 136.

In most cases a thick, curdy precipitate immediately forms. This precipitate is best purified by recrystallization from hot, dilute acid solution. Inasmuch as the alkaloid chloride or bromide frequently separates out in the cold, the recrystallization must be done hot. Obtained under these conditions, the salts crystallized very well. As in the case with the halogen salts of the amines with tellurium, the alkaloids form yellow chlorides with tellurium chloride and red bromides with the bromide.

All of the salts obtained are permanent at the ordinary temperature, but are easily decomposed by heat. Water decomposes them all with precipitation of tellurous acid, while dilute acids readily dissolve them.

Analysis.—In order to determine the composition of the salts, the amount of halogen and tellurium in each was determined and in one salt a combustion for carbon and hydrogen was made. The halogen was determined as the silver salt and the tellurium was determined as element.

CHLORIDES.

Quinine Chlorotellurate, $C_{20}H_{24}N_2O_2 \cdot 2HCl \cdot TeCl_4$.—When a strong solution of tellurium tetrachloride is added to a strong solution of quinine in hydrochloric acid, a light, curdy precipitate forms. This salt can be readily recrystallized from hot dilute hydrochloric acid. It contains no water of crystallization; at 150° it begins to decompose. Water decomposes the substance at the ordinary temperature.

Analysis.—Calculated: Cl, 31.91; Te, 19.12; C, 36.01; H, 3.93. Found: Cl, 31.86, 31.91; Te, 18.55, 18.79; C, 35.77, 35.53, 36.26; H, 3.91, 3.74, 3.72.

Cinchonine Chlorotellurate, $(C_{19}H_{21}N_2O_2 \cdot 2HCl \cdot TeCl_4)$.—This salt forms light yellow crystals.

Analysis.—Calculated: Cl, 33.44. Found: Cl, 33.69, 33.64.

Strychnine Chlorotellurate, $(C_{21}H_{22}N_2O_2 \cdot HCl)_2 \cdot TeCl_4$, appears on recrystallization as large, bright yellow needles.

Analysis.—Calculated: Cl, 21.05; Te, 12.61. Found: Cl, 21.32, 21.03, 21.20, 21.14; Te, 13.13.

Morphine Chlorotellurate, $(C_{17}H_{19}NO_3 \cdot HCl)_2 \cdot TeCl_4$.—This substance appears as dark yellow crystals, and is the most stable of the series toward heat.

Analysis.—Calculated: Cl, 23.30; Te, 13.97. Found: Cl, 23.13, 23.67; Te, 14.21.

Thcobromine Chlorotellurate, $(C_7H_5N_4O_2HCl)_2TeCl_4$.—On bringing together the acid solution of the alkaloid and tellurium tetrachloride, no precipitate appears as with the other substances, but, on standing, the light yellow salt separates.

Analysis.—Calculated: Cl, 30.44; Te, 18.25. Found: Cl, 30.59, 30.55; Te, 18.59.

Brucine Chlorotellurate, $(C_{22}H_{26}N_2O_4HCl)_2TeCl_4$.—This salt appears as light yellow crystals.

Analysis.—Calculated: Cl, 18.81. Found: Cl, 18.36, 18.90.

With aconitine and atropine, non-crystalline bodies were first formed but quickly decomposed.

BROMIDES.

Quinine Bromotellurate, $(C_{20}H_{24}N_2O_2 \cdot 2HBr)_2TeBr_4$.—This salt forms bright red crystals and is easily decomposed by heat.

Analysis.—Calculated: Br, 51.32; Te, 13.67. Found: Br, 51.27, 51.60; Te, 14.09.

Cocaine Bromotellurate, $(C_{17}H_{21}NO_4HBr)_2TeBr_4$.—The salt crystallizes readily in large carmine-red needles. It is quite readily decomposed by heat.

Analysis.—Calculated: Br, 39.47; Te, 10.48. Found: Br, 39.59, 39.14; Te, 11.18.

Brucine Bromotellurate, $(C_{22}H_{26}N_2O_4HBr)_2TeBr_4$.—This salt appears as brick-red crystals.

Analysis.—Calculated: Br, 34.26; Te, 9.12. Found: Br, 34.21, 33.80; Te, 8.50.

Morphine Bromotellurate, $(C_{17}H_{19}NO_3HBr)_2TeBr_4$.—This salt appears as dark red crystals.

Analysis.—Calculated: Br, 40.70; Te, 10.81. Found: Br, 40.42; Te, 10.70.

ON CERTAIN FACTORS INFLUENCING THE PRECIPITATION OF CALCIUM AND MAGNESIUM BY SODIUM CARBONATE.

BY J. M. STILLMAN AND ALVIN J. COX.

Received March 30, 1903.

THE data contained in the following communication were obtained in an investigation undertaken primarily to determine some of the conditions which modify the results of the usual processes

for the purification of water for boiler-feed purposes. In many of the waters of the more or less arid regions of this country the calcium and magnesium salts are present in large quantity, and experience has shown that the usual methods of purification by the use of lime and sodium carbonate give variable results. To determine, if possible, some of the conditions affecting the problem, the experiments here described were undertaken. The data obtained are but a contribution to the problem stated, but they have also application to other than the particular technical problem mentioned.

1. INFLUENCE OF SALTS OF SODIUM UPON THE PRECIPITATION OF CALCIUM AND MAGNESIUM BY SODIUM CARBONATE.

Solutions of calcium chloride and of magnesium chloride were prepared of such concentration that 25 cc. of the calcium solution gave 0.3285 gram calcium oxide, and 25 cc. of the magnesium solution yielded 0.6410 gram magnesium pyrophosphate.

In each test 25 cc. of one of these solutions were placed in a 100 cc. flask, the desired quantity of sodium chloride or sodium sulphate added in the form of a standardized solution, sodium carbonate then added in solution, so that unless otherwise specified 1.2 molecules of sodium carbonate should be present for each molecule of calcium chloride or magnesium chloride present. Larger excess was avoided as being foreign to the problem immediately under consideration. Water was added to make the volume to 100 cc. All conditions of manipulation were made as nearly equal as possible.

A. Influence of Sodium Chloride upon the Precipitation of Calcium.—Two series of tests were made with varying quantities of sodium chloride. In each series, 0, 2, 4, 6, 8 molecules of sodium chloride were added for each molecule of calcium chloride, and then the slight excess of sodium carbonate was added and the flasks filled to 100 cc. One series was then brought to the boiling-point and maintained there for three minutes; the other was not heated. Both series were then allowed to stand at room temperature for seven days.

At the end of this time the contents of the flasks were filtered and the filtrate tested for calcium with ammonium oxalate. No determinable amount of calcium was present, and it was therefore concluded that the presence of sodium chloride has no important

influence upon the precipitation of dilute calcium chloride solutions by sodium carbonate.

B. Influence of Sodium Chloride and Sodium Sulphate upon the Precipitation of Magnesium.—Twenty-five cc. of the above-mentioned magnesium solution were treated in a similar manner with 1.2 molecules sodium carbonate after addition of 0, 2, 4, 6, 8, or 10 molecules of sodium chloride. Duplicate series were prepared as before and one boiled for three minutes, the other not. At the end of seven days' standing the solutions were filtered, the magnesium determined as pyrophosphate in 50 cc. of the filtrate, and the entire amount remaining in solution estimated. The following results were obtained:

Mols. NaCl for 1 mol. $MgCl_2$	$Mg_2P_2O_7$ in sol. per 100 cc.	
	Boiled samples. Gram.	Not boiled. Gram.
0	0.3486	0.4350
2	0.4278	0.4766
4	0.4378	0.4988
6	0.4510	0.5150
8	0.4700	0.5356
10	0.4892	0.5590

Total amount magnesium as $Mg_2P_2O_7$ per 100 cc. before precipitation = 0.6410 gram. The influence of sodium chloride in diminishing the precipitation is here evident, and the brief heating increases the precipitation. It may be here stated that a preliminary experiment similar to the foregoing gave figures showing similar relations. In that test, however, the samples stood but four days, and equilibrium was not sufficiently attained.

With sodium sulphate the following data were obtained, the conditions of experiment being otherwise as with the preceding.

Mols. Na_2SO_4 for 1 mol. $MgCl_2$	$Mg_2P_2O_7$ in sol. per 100 cc.	
	Boiled. Gram.	Not boiled. Gram.
0	0.3486	0.4350
2	0.4846	0.5568
4	0.5816	0.6218
6	0.5874	0.6412 no precipitate.
8	0.5874	0.6406 " "
10 " "

Total amount magnesium as $Mg_2P_2O_7$ per 100 cc. = 0.6410 gram.

The influence of the sodium sulphate is here again well marked, but seems to reach its maximum under the conditions of this experiment at about 6 molecules of sodium sulphate to 1 molecule mag-

esium chloride, and here, as before, the short boiling influences the condition of equilibrium. The curves in Fig. 1 will illustrate

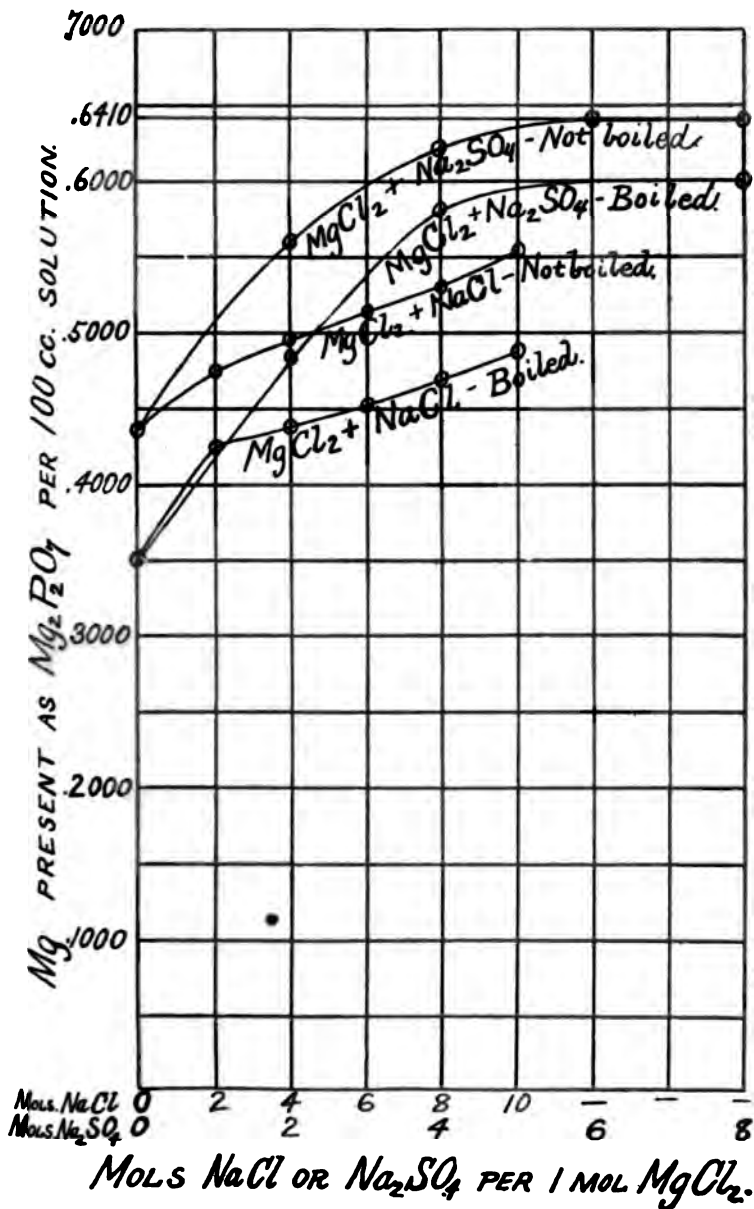


Fig. 1.

these relations. In order to bring out more clearly the relations, equivalent quantities of the two salts are coincident on the abscissas of the curves. It will be noticed that the sodium sulphate appears to exert a greater influence in preventing precipitation than the equivalent quantity of sodium chloride.

II. THE INFLUENCE OF TIME ON PRECIPITATION UNDER VARYING CONDITIONS.

This factor evidently has a direct bearing on the problem of water purification.

A magnesium solution was prepared containing magnesium equivalent to 0.6520 gram $Mg_2P_2O_7$ in 25 cc. The quantities of magnesium precipitated by sodium carbonate at different time intervals were determined under varying conditions.

First.—In solutions maintained at boiling temperature. For this purpose, the solutions were heated in pressure-bottles immersed in a boiling salt-water bath, the temperature of the bath being maintained at 102° – 104° C. Three series were heated in this way.

(a) Twenty-five cc. of the magnesium solution (equivalent to 0.6520 gram magnesium pyrophosphate) were treated with 1.2 molecules sodium carbonate per 1 molecule magnesium chloride, and made up to 100 cc.

(b) Twenty-five cc. were treated as above, after addition of 4 molecules sodium sulphate to 1 molecule of magnesium chloride.

(c) Twenty-five cc. were treated as before, but with 10 molecules of sodium chloride instead of the sulphate. At intervals, the pressure bottles were removed from the bath, the contents thrown on a filter, and 50 cc. of the filtrate used for determination of magnesium. The data are calculated to a basis of 100 cc. of solution.

MAGNESIUM REMAINING IN SOLUTION AS $Mg_2P_2O_7$ PER 100 CC.

Hours.	Gram.	Hours.	Gram.	Hours.	Gram.
After $\frac{1}{4}$	0.1176	$\frac{1}{4}$	0.2246	$\frac{1}{4}$	0.1634
" $\frac{1}{2}$	0.1036	$\frac{1}{2}$	0.1946	$\frac{1}{2}$	0.1498
" 1	0.0740	1	0.0960	$\frac{3}{4}$	0.1322
" 2	0.0164	2	0.0832	1	0.0698
" 3	0.0108	3	0.0726	2	0.0522
"		4	0.0716	3	0.0420
"				$4\frac{1}{4}$	0.0406

These data are shown graphically in Fig. 2.

Second.—The course of the reaction was studied in solutions maintained at room temperature without agitation.

For this purpose flasks containing 700 cc. of the various mix-

tures were immersed in a bath of running water, and the temperature thus kept within a narrow range of variation. At intervals, samples were removed by a pipette and filtered, and the magnesium remaining in solution was determined in 50 cc. of the filtrate.

The magnesium solution used was the same as last described, and the solution of calcium chloride used contained the equivalent of 0.3285 gram calcium oxide per 25 cc. The proportions employed in the different mixtures are given as per 100 cc. of the mixed solutions, though much larger quantities were made up.

The following series of tests were made:

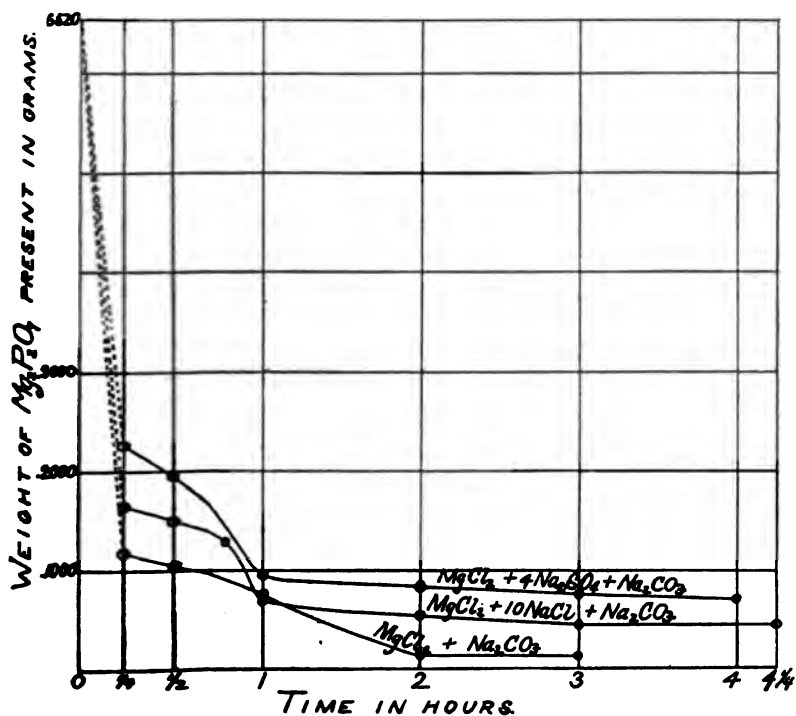


Fig. 2.

A.—Twenty-five cc. of the calcium solution were treated with 1.2 molecules of sodium carbonate and made up to 100 cc.

The calcium as calcium oxide remaining in solution after various time intervals was found as follows:

Of the total 0.3290 gram calcium oxide present, all but about 3 per cent. was precipitated in less than one-fourth hour.

Hours.	Calcium oxide. Gram.
After $\frac{1}{4}$	0.0104
" $\frac{1}{4}$	0.0104
" $1\frac{1}{4}$	0.0100
" 2	0.0083
" 3	0.0076
" $4\frac{1}{4}$	0.0062
" $6\frac{1}{4}$	0.0044
" $8\frac{1}{4}$	0.0032
" $20\frac{1}{4}$	0.0000

B.—The magnesium chloride was treated under the following varying conditions:

(a) Twenty-five cc. with 1.2 molecules of sodium carbonate to 100 cc. solution.

(b) The same mixture with addition of 10 molecules of sodium chloride.

(c) The same with 4 molecules of sodium sulphate.

(d) The same with 10 molecules of sodium sulphate.

Magnesium remaining in solution at varying time intervals as $Mg_2P_2O_7$ per 100 cc. was determined as follows:

Total quantity as $Mg_2P_2O_7$ per 100 cc. of solution was 0.6520 gram.

Hours.	(a). Gram.	(b). Gram.	(c). Gram.	(d).
After 1	0.4152	0.5270	0.5982	No precipitate.
" 3	0.4084	0.5252	0.5832	" "
" $6\frac{1}{2}$	0.4104	0.5216	0.5908	" "
" 12	0.3924	0.5072	0.5760	" "
" 22	0.3782	0.4880	0.5654	" "
" 32	0.3810	0.4882	0.5550	" "
" 46	0.3154	0.4484	0.5560	" "
" $60\frac{1}{2}$	0.2358	0.3966	0.5542	" "
" $80\frac{1}{2}$	0.1634	0.3094	0.5498	" "
" $107\frac{1}{2}$	0.1278	0.2320	0.4824	" "
" $131\frac{1}{2}$	0.1240	0.2204	0.3928	" "

These data are illustrated in the curves of Fig. 3. The variations in temperature are noted on the upper margin of the chart. It will be noticed that the temperature was not quite constant, and this fact may be partly responsible for the irregularities of the curves.

Third.—The influence of continuous agitation upon the course of the reaction.

For this purpose the bottles containing the mixtures were sub-

mitted at room temperature to violent agitation by means of a mechanical shaker operated by a motor. Three series were thus treated:

(a) A magnesium chloride solution containing the equivalent of 0.6871 gram magnesium pyrophosphate per 25 cc. was treated as before with sodium carbonate and diluted to 100 cc. for each 25 cc. of the magnesium solution.

(b) The same mixture after addition of 10 molecules of sodium chloride.

(c) The same mixture after addition of 4 molecules of sodium sulphate.

The shaking was interrupted at intervals for removing samples, and, as before, magnesium was determined in the filtered samples and the results calculated to a basis of 100 cc.

MAGNESIUM AS $Mg_2P_2O_7$ PER 100 CC. SOLUTION UNPRECIPITATED.

Hours.	(a). Gram.	(b). Gram.	(c). Gram.
After 3 $\frac{1}{4}$	0.4364	0.5288	0.6476
" 7 $\frac{1}{2}$	0.4216	0.6384
" 13 $\frac{1}{4}$	0.1684	0.5084	0.6200
" 20 $\frac{1}{4}$	0.1464	0.4092	0.6224
" 34	0.1432	0.2360	0.4316
" 47	0.1364	0.2292	0.3380
" 61	0.1372	0.3260
" 76	0.1368	0.2300	0.3200
" 99 $\frac{3}{4}$	0.1372	0.3320

In the curves in Fig. 3 these data are plotted after recalculating to correspond to a total content before precipitation of 0.6520 gram instead of 0.6871 gram magnesium pyrophosphate per 100 cc., so that the curves may be better compared with the other data given on the chart. On the same diagram are also reproduced for comparison the data of Fig. 2. Comparison of these curves will show that in every case the influence of the presence of sodium chloride or sulphate is to diminish the precipitation of magnesium by sodium carbonate, and in these tests the sulphate exerts a greater influence in this direction than an equivalent quantity of the chloride. It would be premature, however, to draw any sweeping quantitative generalizations from these few comparisons. Even attempts to duplicate as exactly as possible the conditions of such a series as any one of the above, so far as our experience goes, do not give the same quantitative relations. The reason for this is easily seen in the difficulty of equalizing all conditions to which the

establishment of equilibrium is sensitive. On the other hand, the general relations of the influence of the above-mentioned salts and of temperature and agitation upon the precipitation of magnesium by sodium carbonate seem to be quite clearly established.

It is well-known that for the separation of magnesium in water-purification, calcium hydroxide is a much more effective precipitant than sodium carbonate. In order to obtain an approximate notion of the relation of this reaction to such data as above obtained, a single series of experiments was executed.

A magnesium chloride solution was treated with a clear solution of calcium hydroxide (free from alkalis), with and without the presence of sodium chloride, and the same quantities of the same

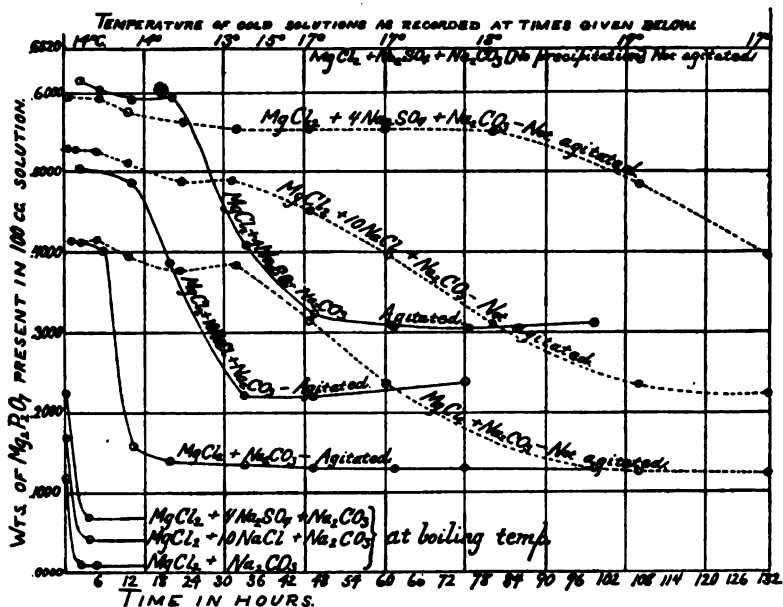


Fig. 3.

solution were treated under the same conditions with an equivalent quantity of sodium carbonate. Owing to the greater insolubility of calcium hydroxide, it was necessary to use a more dilute magnesium solution.

The magnesium solution contained 0.2063 gram as $Mg_3P_2O_7$ in 3.750 cc.

The calcium hydroxide solution contained 0.00144 gram as CaO per cubic centimeter.

Mixtures were made as follows:

(a).	(b).	(c).	(d).
3.75 cc. $MgCl_2$	3.75 cc. $MgCl_2$	3.75 cc. $MgCl_2$	3.75 cc. $MgCl_2$
77.75 cc. CaO (1.1 mol.)	do.	4.07 cc. Na_2CO_3	(1.1 mol.) do.
18.50 cc. H_2O	18.50 cc. $NaCl$ (10 mol.)	92.18 cc. H_2O	18.50 cc. (10 mol.) $NaCl$
			73.68 cc. H_2O
100.00	100.00	100.00	100.00

The data are here given per 100 cc., although larger quantities (400 cc.) were actually used. These solutions were kept agitated by the mechanical shaker at room temperature and sampled at intervals. The following quantities of magnesium pyrophosphate per 100 cc. were found in the filtered samples.

Total amount of $Mg_2P_2O_7$ per 100 cc. is 0.2063 gram.

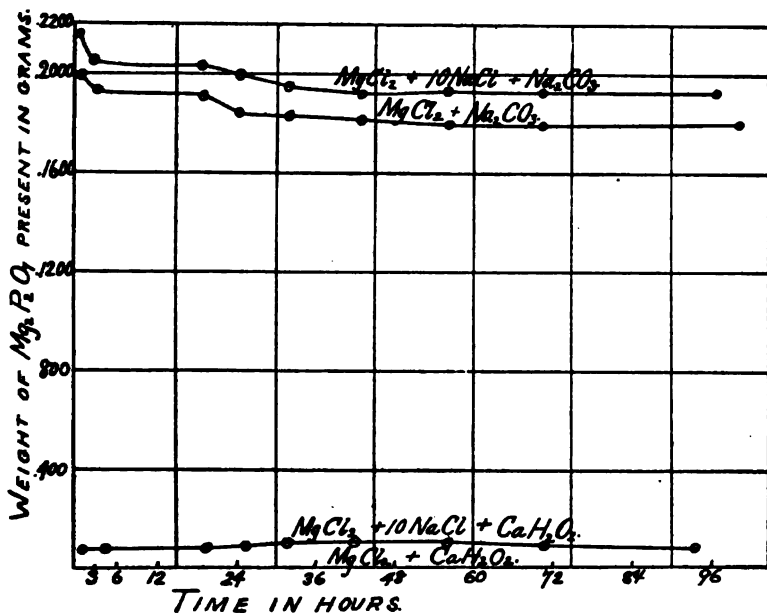


Fig. 4.

Hours.	(a). Gram.	(b). Gram.	(c). Gram.	(d). Gram.
After 1 1/4	0.1984	0.2124
" 1 1/2	0.0080
" 1 3/4	0.0000
" 4 1/2	0.0000	0.0076	0.1936	0.2048
" 19 1/2	0.0000	0.0072	0.1908	0.2028
" 25 1/2	0.0000	0.0080	0.1844	0.1996
" 31 3/4	0.0000	0.0100	0.1828	0.1956
" 43 1/2	0.0000	0.0096	0.1820	0.1928
" 56 1/2	0.0000	0.0084	0.1788	0.1928
" 71	0.0000	0.0080	0.1780	0.1928
" 93 3/4	0.0000	0.0080	0.1928
" 99 3/4	0.0000	0.1792

The foregoing data are produced graphically in Fig. 4. It will be noted that sodium chloride appears to have some influence on the precipitation of magnesium by calcium hydroxide, but that nevertheless the precipitation is quite complete. In the parallel tests with sodium carbonate, the amount of magnesium held in solution by sodium chloride is less in proportion to the entire amount present than was the case in the preceding experiments with solutions of somewhat greater concentration. In the more dilute solution, only about 6 per cent. of the magnesium present was held in solution, while in the less dilute about 15 per cent. was held in solution by 10 molecules of sodium chloride.

There is no intention to draw any generalizations from the single experiment with calcium hydroxide. Other experiments are in progress in this laboratory which may form the subject of a further communication on similar lines.

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THE DETERMINATION OF CARBONIC ACID IN DRINKING-WATER.

BY FRED B. FORBES AND GILBERT H. PRATT.

Received April 27, 1903.

IN the course of an investigation of the action of the various public water supplies of Massachusetts upon metallic pipes, it became desirable to know the amount of free carbonic acid contained in these waters at different times, as the results of many experiments indicated that this substance was in a large measure responsible for the action of water upon pipes, especially those of lead.¹

Carbonic acid, as is well known, may exist in natural waters in three forms: Fixed carbonic acid combined directly with the alkaline earth bases, calcium oxide and magnesium oxide, to form normal carbonates, half-combined carbonic acid, and free carbonic acid.

The actual existence of bicarbonates of calcium and magnesium in solution has never been absolutely proven, as these salts have never been isolated; but for all practical purposes these compounds may be assumed to exist, as the behavior of the normal carbonates in solution in the presence of an excess of carbonic acid leads strongly to this conclusion.

¹ Report of Massachusetts State Board of Health, 1898, 541; 1900, 487.

If more carbonic acid than is necessary to form bicarbonates with the alkaline earth bases is present, it remains dissolved in the water in the free state, and is generally considered as a true acid with the formula H_2CO_3 .

When a water containing free and half-bound carbonic acid is heated, the free acid is easily driven off. On boiling, the half-bound acid may also be expelled, though completely with some difficulty, resulting in the precipitation of the normal carbonate with which it was combined.

The method for the determination of carbonic acid originally used in the investigation was the well-known Pettenkofer method,¹ which determines the sum of the free and half-bound. For the separation of the free from the half-bound, a modification devised by Dr. T. M. Drown and which will be described later was employed. It was early seen that in the Pettenkofer method, when carried out as directed in most works on analytical chemistry, there were several sources of considerable error, and some modifications were introduced in order to avoid these errors.

During the course of our work the very excellent paper on "The Estimation of Carbonic Acid in Water" by J. W. Ellms and J. C. Benecker² appeared, recommending the Lunge-Trillich or Seyler method,³ and experiments were made by us with this method, and also with the method of boiling off the carbonic acid directly, and absorbing in potash bulbs. This latter method is not practicable from a water analyst's point of view, as it requires an apparatus too complicated for use in the field, and all determinations of free carbonic acid to be of value must be made at the source of supply, as a water, after being drawn, very soon loses a considerable part of its dissolved carbonic acid. This method has been used, however, as a check on the other two, in experiments upon natural waters whose carbonic acid contents were unknown.

It is the purpose of the following pages to give an account of a series of results obtained with the three methods, and to point out some of the errors in each.

THE PETTENKOFER METHOD.

The usual mode of procedure is given by Sutton⁴ as follows: "100 cc. of the water are put into a flask with 3 cc. of a strong

¹ *N. Rep. Pharm.*, 10, 1.

² *This Journal*, 23, 405 (1901).

³ *Chem. News*, 70, 104 (1894); *Analyst*, 22, 312 (1897).

⁴ "Volumetric Analysis," 7th edition, 1896, p. 96.

solution of calcium or barium chloride, and 2 cc. of saturated solution of ammonium chloride; 45 cc. of baryta or lime-water, the strength of which is previously ascertained by means of decinormal acid, are then added, the flask well corked and put aside to settle; when the precipitate is fully subsided, take out 50 cc. of the clear liquid with a pipette, and let this be titrated with decinormal acid. The quantity required must be multiplied by 3 for the total baryta or lime-water, there being only 50 cc. taken; the number of cubic centimeters so found must be deducted from the quantity required for the baryta solution added; the remainder multiplied by 0.0022 will give the weight of carbonic acid existing as free and as bicarbonate in the 100 cc. The addition of the barium or calcium chloride, and the ammonium chloride is made to prevent any irregularity which might arise from alkaline carbonates or sulphates or from magnesia."

The reactions which take place between the barium and ammonium chlorides and magnesium are fully explained in Fresenius' "Quantitative Analysis,"¹ and will not be repeated here.

There are a great many precautions which must be observed in order to obtain results that are at all reliable. Among the principal of these are the avoidance of exposure to the air of the barium hydroxide solution and of the sample of water at all times. especially during the titration, the use of a siphon to introduce the sample of water into the ground glass-stoppered bottle in which the precipitation is made, the addition of ammonium chloride during the standardization of the barium hydroxide solution, if rosolic acid is used as an indicator, and the allowance of a sufficient time for the separation of the carbonates in crystalline form before withdrawing the supernatant liquid for titration.

In carrying out this method according to the above directions, even with a strict observance of all the precautions noted, there are several sources of considerable error that do not seem to be generally recognized. They are due to the fact that working on such a small quantity of water as 100 cc. and employing N/10 acid, very slight errors in the titration of the aliquot portion of 50 cc., in measuring out the sample for titration and in measuring the original sample, make a considerable difference in the final result.

Long practice with the method has convinced us that it is impossible to titrate much closer than 0.05 cc., due principally to the

¹ Fresenius' "Quantitative Analysis," English edition, 1889, p. 405.

fact that the best indicator that we can use, rosolic acid, is somewhat affected by ammonium salts, and the end-point is a little uncertain. Suppose, for example, that our barium hydroxide is exactly $N/10$, 45 cc. equaling 45 cc. of our sulphuric acid, that our measurements are correct, and that after carrying out the process according to Sutton's directions we obtain a reading of 14.40 cc. acid for the aliquot portion of 50 cc. which we titrate. A simple calculation shows this to be equivalent to 3.96 parts per 100,000 carbonic acid in the original sample. Suppose that instead of 14.40 cc. our acid reading had been 14.35 cc.; then a similar calculation shows this to be equivalent to 4.29 parts, as against 3.96 in the first case. This is not only an error of 8.3 per cent. on the value 3.96, but is an absolute difference of 0.33 part on any value, due to this one source of error.

In order to lessen the effect of all three of these errors, we have modified the details of the method as follows:

Ground glass-stoppered bottles of 16-ounce capacity, holding approximately 480 cc., are accurately calibrated by weighing completely filled with water. The bottle is filled with the water to be analyzed by means of a siphon, the glass stopper inserted leaving no air bubble, and the neck of the bottle wiped dry. The glass stopper is then carefully removed, and 57 cc. of the water withdrawn by means of an accurately calibrated pipette, in order to make room for the reagents. Three cc. of strong barium chloride solution (8 grams per liter), 2 cc. of saturated ammonium chloride solution, and 50 cc. of standard barium hydroxide are then introduced, the bottle quickly stoppered, well shaken, and set aside to settle.

There is now in the bottle an air space of only 2 cc., which is left to avoid the possibility of loss of liquid when the stopper is inserted. After the precipitated carbonates have completely settled out, several portions of 100 cc. are siphoned off and titrated with $N/50$ sulphuric acid, which is prepared from our $N/10$ acid, against which the barium hydroxide is standardized, by carefully diluting with water freed from carbonic acid by boiling. The barium hydroxide that we use is approximately $N/15$, and is carefully preserved out of contact with the air, the bottle in which it is kept being fitted with an arrangement whereby the air is drawn through soda-lime before entering either the bottle or the burette. The figure obtained by averaging several results of titration of portions of 100 cc. is taken as the true value.

The use of this large quantity of water and the titration of 100-cc. portions reduce considerably the errors due to the difficulty of obtaining the exact end-point, and those due to inaccuracies of measurement.

The decrease in the concentration of the barium hydroxide solution, due to the increase in the volume of our sample, renders it necessary, in some cases, to allow a longer time than is usually given for the complete precipitation of the carbonates. Standard solutions of free or of combined carbonic acid seem to settle out well on standing over night (that is, twelve to sixteen hours), but some natural waters require longer. We have generally found that samples made up in the afternoon of one day and titrated in the morning of the second day after, have stood a sufficiently long time.

The following table shows one of many series of results obtained by our method with standard solutions of sodium carbonate half neutralized with sulphuric acid.

CARBONIC ACID. (Parts per 100,000.)

Taken.	Found.	Average.	Error. Per cent.
1.10	0.99	1.05	4.5
1.10	1.05		
1.10	1.06		
1.10	1.08		
2.20	1.98	2.14	2.7
2.20	2.15		
2.20	2.23		
2.20	2.20		
3.30	3.12	3.17	4.0
3.30	3.21		
4.40	4.21	4.22	4.0
4.40	4.15		
4.40	4.23		
4.40	4.28		

These samples all stood twenty-four hours before titrating, and the carbonic acid was all in the half-combined state. A great many experiments were also performed in which the sodium carbonate was completely neutralized by sulphuric acid, thus giving all the carbonic acid in the free state. These results were invariably lower than the results on half-bound, due undoubtedly to loss of free carbonic acid during manipulation.

In order to see if more complete precipitation could be ob-

tained by allowing the samples to stand a longer time, the following series of determinations was made:

CARBONIC ACID. (Parts per 100,000.)

Time stood. Hours.	Taken.	Found.
18	2.20	2.25
66	2.20	2.16
113	2.20	2.07

Average, 2.16

It is seen that the shortest period of the three gave complete precipitation, thus showing that the cause of low results in our first table was not because of insufficient time allowed for the carbonates to separate out.

The following table shows a series of determinations of carbonic acid in natural waters, and in the same waters after the addition of known amounts of carbonic acid (as half-bound).¹

(Parts per 100,000.)

Water No.	CO ₂ added.	Total found.	Mean.	Parts added found.
1.....	0.00	1.15	1.21	2.31
	0.00	1.27		
	2.20	3.51	3.52	
	2.20	3.52		
2.....	0.00	1.43	1.51	2.08
	0.00	1.58		
	2.20	3.61	3.59	
	2.20	3.56		
3.....	0.00	1.32	1.27	2.27
	0.00	1.21		
	2.20	3.54	3.54	
	2.20	3.54		

Average, 2.22

SEPARATION OF FREE FROM HALF-BOUND.

In order to separate the free from the half-bound carbonic acid, Dr. T. M. Drown has devised the following apparatus: A piece of glass tubing about 2.5 feet long and $\frac{5}{8}$ of an inch in diameter, drawn out at one end to a small aperture, is inserted through a rubber stopper into the mouth of an aspirator bottle having a side tubular. The glass tube is filled with gravel about the size of peas. A strong current of air is drawn down through the gravel by means of an aspirator or pump, while the water is slowly dropped

¹ Half-bound added instead of free in order to avoid loss of free carbonic acid in making up solutions.

into the tube at the top from a separatory funnel at the rate of about two drops a second. The water collects in the bottle, and when in sufficient quantity is withdrawn, and the half-bound carbonic acid determined by the Pettenkofer method as before. By this means the free carbonic acid is eliminated from the water, while the half-bound is unaffected. If the water is very high in free carbonic acid, it might be necessary to pass it through the column a second time, but for most waters once is sufficient. The loss in volume due to evaporation has been found to be only about 1 per cent., with a vacuum of 2.5 pounds, and may be neglected in most instances. The following table shows a series of results on standard solutions made by wholly or partially neutralizing solutions of sodium carbonate with sulphuric acid.

SEPARATION OF FREE FROM HALF-BOUND CO_2 . (Parts per 100,000.)

Taken.		Found.		Remarks.
Free.	Half-bound.	Half-bound.	Mean.	
4.40	2.20	2.22	2.25	{ Aspirated 2 drops per second.
4.40	2.20	2.27		{ " 2 " " "
4.40	2.20	2.31	2.30	{ " 1 drop " "
4.40	2.20	2.28		{ " 1 " " "
4.40	2.20	2.17	2.18	{ " twice, 2 drops per second.
4.40	2.20	2.19		{ " " 2 " " "
1.10	1.67	1.90	1.84	{ " 2 drops per second.
1.10	1.67	1.77		{ " 2 " " "
0.00	2.20	2.31	2.31	{ " 2 " " "
0.00	2.20	2.30		{ " 2 " " "
1.10	1.10	1.22	1.22	{ " 2 " " "
1.10	1.10	1.21		{ " 2 " " "
2.20	1.10	1.05	1.12	{ " 2 " " "
2.20	1.10	1.19		{ " 2 " " "
2.20	2.20	2.36	2.34	{ " 2 " " "
2.20	2.20	2.31		{ " 2 " " "

Care must be taken to keep the water dropping at a uniformly slow rate, and to keep the current of air drawing steadily through the tube. If the free carbonic acid is not all expelled, then, of course, the half-bound result is high, and the figure for free, being obtained by subtracting the half-bound from the sum, is naturally low. With careful work, however, the method gives very good results, and is more convenient than the modification of the Pettenkofer method introduced by Trillich in order to accomplish the separation of the free from the half-bound.

THE LUNGE-TRILLICH OR SEYLER METHOD.

This method is very completely discussed in the paper by Ellms and Beneker, and is recommended by them as preferable to any other volumetric method for the determination of free and half-bound carbonic acid in natural water. It depends upon the assumption that in the bicarbonates of the alkaline earth bases there is 1 molecule of half-bound carbonic acid for each molecule of fixed, and that these bicarbonates are neutral to phenolphthalein.

When a solution containing free carbonic acid is titrated with sodium carbonate, with phenolphthalein present as an indicator, sodium bicarbonate is formed; this being neutral to phenolphthalein, as soon as all the free carbonic acid is used up, any further addition of sodium carbonate produces a pink color. Thus the free carbonic acid is obtained directly. By a determination of the fixed carbonic acid by Hehner's¹ process, the half-bound is obtained, as we have assumed this to equal the fixed when the water is acid to phenolphthalein.

When the water is alkaline to phenolphthalein, the phenolphthalein alkalinity is first determined, and then the total alkalinity with lacmoid or methyl orange, according to Hehner's process. Twice the phenolphthalein alkalinity subtracted from the total alkalinity gives the half-bound carbonic acid, no free acid being present in this case, and the half-bound being less than the fixed—that is, some of the normal carbonates are held in solution without the aid of any half-bound.

If no free carbonic acid is present, the half-bound may equal the fixed, and the water will be neutral to phenolphthalein. There is another condition in which carbonic acid might occur in a free state which is mentioned by Seyler, but which would occur so rarely in a natural water that it is hardly necessary to consider.

The mode of procedure is as follows: For the determination of the free carbonic acid, 100 cc. of the sample are introduced into a tall glass cylinder (a 100 cc. nitrite tube) by means of a siphon, 5 or 6 drops of a neutral alcohol solution of phenolphthalein of the usual strength added, and N/50 sodium carbonate run in from a burette with careful stirring, until a permanent faint pink color is obtained. If the water is high in free carbonic acid, it is better to take less than 100 cc., and in any case, great care must be exercised in manipulation, especially in not stirring too

¹ Ellms : *This Journal*, 21, 359 (1899).

vigorously, in order to avoid loss of carbonic acid; on the other hand, the titration should be quickly completed in order to avoid absorption of carbonic acid from the air, which readily takes place during the end of the reaction. Great care is necessary in the standardization of the solutions and in their preservation, in order to avoid absorption of carbonic acid.

For the determination of the fixed carbonic acid, from which the half-bound is calculated, the well-known method of Hehner is employed. The writers prefer methyl orange as an indicator.

The following table shows the action of sodium carbonate solutions with the two indicators, when titrated with sulphuric acid.

Solution No. 1.			Solution No. 2.		
cc. H ₂ SO ₄ .			cc. H ₂ SO ₄ .		
cc. Na ₂ CO ₃ .	Methyl orange.	Phenolphthalein.	cc. Na ₂ CO ₃ .	Methyl orange.	Phenolphthalein.
10	9.75	4.85	10	9.65	4.78
10	9.67	4.90	10	9.62	4.80
10	9.73	4.85	10	9.63	4.80
10	9.70	4.84
10	9.75	4.89
Average,	9.72	4.87		9.63	4.80

With phenolphthalein as an indicator, only half the quantity of acid is required to give an end-point as with methyl orange.

THE DIRECT METHOD.

This method for the determination of carbonic acid consists in boiling off the gas in a suitable apparatus, fitted with a return-flow condenser and drying tubes, and absorbing the carbonic acid in a weighed potash bulb or soda-lime tube. Various modifications of the apparatus have been employed by different workers, but the form that we have found quite satisfactory is constructed as follows: A liter, round-bottomed flask, supported on a lamp-stand, contains the sample of water, and a perforated rubber stopper fits tightly into the neck of this flask. Through one perforation passes a return-flow condenser, while through the other passes a tube bent so as to form a water-seal, and carrying at its upper end a small separatory funnel.

The return-flow condenser is a tube about 24 inches long and 0.5 inch in diameter for 7 inches of the lower end and 5 inches of the upper end, while the main body of the tube is 1 inch in diameter, and is surrounded by a water-jacket. This form of tube is employed in order to give a large condensing surface.

A small delivery tube conducts the carbonic acid gas through a U-tube containing glass beads moistened with sulphuric acid, thence through another U-tube containing fused calcium chloride, thence to the potash bulb. Beyond the potash bulb is a tube containing soda-lime, to remove carbonic acid from any air accidentally drawn back into the bulb during the process.

Before each analysis the apparatus is freed from carbonic acid by boiling water in the flask, and aspirating while cooling, until the bulb weighs constant. When the flame is removed, an aspirator is attached to the last tube, in order to draw through any carbonic acid which may be present, and to equalize the pressure before disconnecting the bulb. All the air which enters the apparatus is drawn through a Liebig bulb containing caustic potash solution and connected with the separatory funnel.

The free and half-bound carbonic acid are thus determined together in this apparatus. In order to differentiate, the fixed may be decomposed by sulphuric acid introduced by means of the separatory funnel after the free and half-bound are expelled, and the carbonic acid evolved absorbed in the weighed bulb as before.

From these data, the half-bound acid may be calculated.

The following table shows a few results by this method on standard solutions. In order to avoid loss of carbonic acid, they were prepared by measuring into the flask the required amount of dilute sulphuric acid, then introducing the weighed amount of sodium carbonate wrapped in a bit of paper. Before the reaction could take place, the flask was quickly stoppered.

CARBONIC ACID. (Parts per 100,000.)

Taken.			Found.		
Free.	Half-bound.	Sum.	Free.	Half-bound.	Sum.
3.30	3.20
4.40	4.47
4.40	4.40
4.40	4.40
2.93	1.47	4.40	4.30
3.23	0.59	3.82	3.60
1.47	1.47	2.94	1.47 ¹	1.20	2.67
2.93	1.47	4.40	3.07 ¹	1.13	4.20
1.47	1.47	2.94	1.73 ¹	1.27	3.00
5.87	2.93	8.80	8.53
5.87	2.93	8.80	...	3.00	...

¹ In every case the sum of the free and the half-bound acid is determined first, and then the fixed, from which the half-bound is calculated. The free is thus always obtained by difference, and any error in either the sum or the half-bound affects the free result; in fact, these errors are frequently in the same direction, so that the accuracy of the free result is not as great as that of the other figures.

These results show the method to be capable of giving fairly accurate results, on standard solutions, at least, especially when the carbonic acid is all in the free state. When there is half-bound also present, it is somewhat more difficult to obtain accurate results, the tendency being for them to be low on account of the difficulty of expelling the last traces of half-bound carbonic acid. A source of some trouble in the method when a potash bulb is used is the tendency of the potash solution to go over into the drying tube, due to the strong suction which it is necessary to apply in order to keep the current moving always in the right direction.

In working with natural waters, this method has been applied only to clear and colorless waters containing little organic matter, as according to some writers, in some waters, especially those which are polluted with sewage,¹ decomposition of unstable organic matter at the boiling temperature may liberate free carbonic acid.

COMPARATIVE DETERMINATIONS BY ALL THREE METHODS ON NATURAL WATERS.

In experiments on standard solutions with various methods of determining carbonic acid, the conditions are quite different from those obtained in actual practice, as it is impossible to prepare the standard solutions so that they are similar in composition to natural waters, since the composition of the natural waters in which we are called upon to determine carbonic acid varies greatly. For this reason a series of results obtained by any method, in solutions of carbonic acid in distilled water does not necessarily determine to what degree of accuracy the method may be relied upon in actual practice. This is especially true of the Seyler method, as the titration of solutions of carbonic acid made by partially or completely neutralizing sodium carbonate solutions with sulphuric acid amounts to little more than a restandardization of the solutions. The errors that are found in such results are the errors of standardization and of manipulation in making up the solutions. Also, in both the Pettenkofer and the Seyler methods the principal cause of low results on free carbonic acid is due to the loss which unavoidably occurs before the method can be fairly applied.

The following table shows a series of determinations on natural waters of varying composition:

¹ Burghardt : *Chem. News*, 1887, p. 121.

CARBONIC ACID. (Parts per 100,000.)							
Water No.	Seyler.			Modified Pettenkofer. ¹			Direct boiling. Sum.
	Free.	Half-bound.	Sum.	Free.	Half-bound.	Sum.	
1	1.98	0.57	2.55	2.60	2.53
2	2.02	0.62	2.64	1.90	0.69	2.59	2.40
3	0.75	0.70	1.45	1.25	...
4	1.01	0.57	1.58	0.21	0.48	0.69	1.47
5	1.10	1.32	2.42	1.92	2.67
6	0.79	0.53	1.32	1.13	1.20
7	0.97	1.10	2.07	1.05	1.19	2.24	...
8	0.70	0.97	1.67	0.84	0.70	1.54	...
9	1.76	1.28	3.04	1.84	1.34	3.18	...
10	0.57	1.23	1.80	0.77	1.07	1.84	...
11	0.26	0.26	0.52	0.13	0.44	0.57	...
12	2.20	0.44	2.64	2.19	0.61	2.80	...
13	0.57	0.26	0.83	0.51	0.33	0.84	...
14	0.75	0.53	1.28	0.32	0.77	1.09	...
15	0.75	1.85	2.60	0.99	1.57	2.56	...
16	0.92	1.45	2.37	0.88	1.18	2.06	...
17	0.84	1.32	2.16	0.93	1.02	1.95	...
18	0.26	0.40	0.66	0.15	0.34	0.49	..
19	0.70	0.31	1.01	0.45	0.28	0.73	...
20	0.04	1.41	1.45	0.11	0.83	0.94	...
21	0.88	1.06	1.94	1.00	0.64	1.64	..
22	0.97	0.66	1.63	1.18	0.24	1.42	...
23	2.64	0.48	3.12	0.91	0.31	1.22	...
24	0.62	0.70	1.32	0.65	0.20	0.85	...
25	2.29	1.45	3.74	3.66	...
26	2.86	0.31	3.17	1.85	...
27	1.94	1.01	2.95	2.36	...
28	1.94	0.92	2.86	2.87	...

It is a rather difficult matter to make comparisons of the two principal methods, the Seyler and Pettenkofer, for the following reasons: All the waters were acid to phenolphthalein and so by the Seyler method the free carbonic acid was phenolphthalein and so by the Seyler method the free acid was determined directly, and the half-bound calculated from the fixed, which is determined by *Hehner's method*. Thus, the free and the half-bound represent actual determinations, while the sum is naturally obtained by adding these two results together. In our modification of the Pettenkofer method, on the other hand, the sum and the half-bound represent actual determinations, while the free is obtained by difference. It is thus seen that the only one of

¹ Free expelled by aspirating, and the half-bound determined; this figure subtracted from the sum to give the free.

the three figures which represents an actual determination in both methods is the figure for half-bound; and unfortunately, in one method, the Seyler, this figure is obtained independently of the free, while in our modification of the Pettenkofer method this figure is dependent on the thoroughness with which the free is expelled by aspiration.

A study of the table shows the following facts:

1. In seven out of twenty cases in which complete results were obtained by both methods, no result by either method differs from the corresponding result by the other method by over 0.20 of a part. This is a large percentage difference, to be sure, when the figure is low, but is a small absolute difference when the opportunities for error are considered, and as far as our present knowledge of the significance of carbonic acid in a drinking-water goes, such small differences are not important.

2. Considering only the half-bound results, as these figures are more nearly comparable in both methods, it is seen that in thirteen out of twenty cases, in which the half-bound was determined, the Seyler result is higher than the modified Pettenkofer. This seems to indicate that the method of separation of the free from the half-bound by aspiration in the modified Pettenkofer method can be relied upon for sufficient accuracy.

3. Considering the figures for the sum of the free and half-bound obtained by both methods, it is seen that in twenty instances out of twenty-eight in which the sum was determined, the result by the Seyler method was higher than that by the modified Pettenkofer. In experiments Nos. 1, 2 and 6, the results on the sum of the free and half-bound by three methods vary less than 0.10 part from the average of the three figures.

4. Considering the free results, it is seen that out of twenty determinations, the Seyler method gave higher results in ten, or just half.

From these few comparisons it appears that the Seyler method tends to give higher results than the modified Pettenkofer, and that these higher results are nearer the true value is shown by the results obtained by the boiling method, and also by the experiments on standard solutions.

To know the amount of the carbonic acid that is in the free state is of the most importance to the water analyst, so it is the result on the free acid that really deserves the most attention.

It will be seen from the table that, although half the free results by the modified Pettenkofer method are higher than those by the Seyler, yet there are some results which are erratic. For example, in experiment No. 4, the sum by the Seyler method checks well with the result obtained by the boiling method, and the results on half-bound by both the Seyler and the modified Pettenkofer methods agree well, yet the sum, and hence the free which depends upon it, is much lower in the modified Pettenkofer than in the Seyler. This is only one example among many similar ones which have occurred and which we have not given in our table.

The cause of these erratic results which frequently occur in the Pettenkofer method is not apparent from any of our experiments. It is a well-known fact that magnesium is liable to influence the results somewhat, but whatever might be learned by experiments with standard solutions containing magnesium, our experience has shown that the erratic results frequently obtained by this method with natural waters cannot often be traced directly to this element.

Considering the experiments of other investigators, together with those which we have performed, it seems that there is something to be said in favor of each method. Both methods require the utmost care in manipulation, this being especially true of the Seyler method for the determination of free carbonic acid. The advantages of the Pettenkofer method seem to be the less liability to loss or absorption from the air of free carbonic acid during the determination of the sum or half-bound, while the longer time and more apparatus required to complete the determination constitute a disadvantage. In regard to accuracy, the results are generally somewhat low, especially with waters low in carbonic acid, and frequent erratic results are obtained. The presence of magnesium salts is also a possible source of difficulty.

The Seyler method has the advantage of convenience and quickness of execution, but the determination of the free carbonic acid by titration with phenolphthalein as an indicator is a matter of considerable uncertainty, and under some conditions, of difficulty. Disturbances due to the presence of magnesium salts are avoided in this method, and the determination by Hehner's method of the fixed, from which the half-bound is calculated, is satisfactory. The results by this method are liable to be somewhat low, but not as low as those by the Pettenkofer.

Neither method can be relied upon to give results always within

a certain percentage of the true values, and thus neither has a preeminent claim to scientific accuracy; for practical work in water analysis, however, the Seyler method, in the hands of an experienced operator, especially on account of rapidity of completion, has much to commend itself, and it is our purpose to employ it in our regular work.

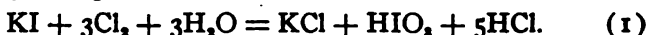
MASSACHUSETTS STATE BOARD OF HEALTH,
LABORATORY FOR WATER ANALYSIS, BOSTON, MASS.

TITRATIONS WITH POTASSIUM IODATE.

BY LAUNCELOT W. ANDREWS.

Received May 23, 1903.

As is well known, when potassium iodide is titrated with chlorine water in a neutral solution, the reaction which takes place is expressed by the equation:



On the other hand it may not be so well known that if a large excess of free hydrochloric acid is present during the titration, chloroform or carbon tetrachloride being used as before for an indicator, the reaction will be



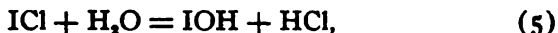
In both cases the end of the reaction is shown by the immiscible solvent becoming colorless. If instead of chlorine water we titrate with a solution of potassium iodate, the stage at which the reaction stops is likewise dependent upon the concentration of the acid. If this be low, the reaction goes no further than to set the iodine free in accordance with the equation



while if a great excess of hydrochloric acid is present the reaction runs



the immiscible solvent remaining violet in the former case (No. 3), but in the latter becoming colorless, while the supernatant solution turns bright yellow from the iodine chloride. The probable explanation of this behavior is that iodine chloride, as the salt of a very weak base, undergoes hydrolysis in a neutral or feebly acid solution, with the production of the corresponding hydroxide and acid; thus,



the iodos hydroxide ("hypoiodous acid"), which is formed, undergoing spontaneous conversion into iodic acid, etc., whereas the hydrolysis is prevented by a great excess of hydrochloric acid.

The reaction of equation (1) was used long ago by A. and F. Dupré¹ for the titration of iodides. In order to compare the reactions of the first two equations, I titrated 5 cc. of a decinormal potassium iodide solution with chlorine water in presence of 5 cc. of chloroform. After the addition of 75.4 cc. of the latter the chloroform became colorless. The titration was now repeated with the further addition of respectively 15, 20 and 30 cc. of strongest hydrochloric acid and the amounts of chlorine water required were, 25.4, 25.22 and 25.25 cc., the end reaction being of extraordinary sharpness. Nearly three times as much chlorine was, therefore, required in the absence of hydrochloric acid as in its presence, as the theory demands. Probably, if the small amount of acid produced by the reaction itself (equation 1) had been neutralized by the addition of calcium carbonate, the theoretical amount of 75.75 cc. of chlorine solution would have been required. In order to judge the influence of smaller quantities of acid, the titration was repeated with addition of 1, 2, 5 and 10 cc. of concentrated hydrochloric acid, when respectively 34.1, 26.9, 26.0 and 25.6 cc. of chlorine water were required.

From these preliminary experiments, it appeared that the hydrolysis of the iodine chloride might be wholly inhibited by addition of a sufficiency of acid and that a solution of potassium iodate might be successfully substituted for the chlorine water, thus realizing the reaction of equation 4. 9.7465 grams of acid potassium iodate were dissolved in water and made up to 1 liter. According to the theory, each cubic centimeter of this solution should be equivalent to 16.6 mg. of potassium iodide. To 10 cc. of a solution of pure potassium iodide (20.6 grams to the liter), 5 cc. of chloroform, 20 cc. of water and 30 cc. of concentrated hydrochloric acid (sp. gr. 1.21) were added and the mixture was titrated in a glass-stoppered bottle of 250 cc. capacity, with the iodate solution, shaking briskly, until the chloroform lost its color, the end-point being exceedingly sharp. 12.43 cc. of the iodate solution were required. Hence, 0.20634 gram potassium iodide was found against 0.20600 taken, or 100.17 per cent. In a second ex-

¹ *Ann. Chem. (Liebig)*, 94, 365 (1855).

periment, 15 cc. of the iodide solution titrated in the same way with 33 cc. of hydrochloric acid and no additional water, required 18.62 cc. of the iodate solution, corresponding to 0.30900 gram found, against 0.30900 gram taken, or 100.00 per cent., found.

The process as described can be applied to the titration of chromates. For this purpose the chromate is added to an excess of a titrated potassium iodide solution, with 5 cc. of chloroform and sufficient concentrated hydrochloric acid to be at least half the volume of the entire mixture at the close of the titration. The titration is then carried out precisely as described above. In one experiment of this sort, 36.3 mg. of potassium pyrochromate were taken and 36.8 mg. found.

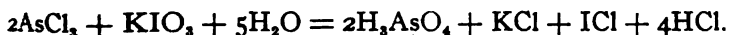
The following experiment shows the applicability of the process to the titration of free iodine: 0.3447 gram of pure iodine was weighed and placed in the stoppered bottle previously used, with 5 cc. of a potassium iodide solution containing 20.6 grams per liter, 10 cc. of fuming hydrochloric acid and 5 cc. of chloroform were added, and the titration was carried out in the usual way. Required: 19.85 cc. of standard iodate. Since 6.20 cc. are required for the iodide, 13.65 cc. remain as corresponding to the free iodine, or 0.3467 gram iodine found; 100.46 per cent.

To determine whether the method can be used for determination of chlorates, and under what conditions, the succeeding experiments were tried. Five cc. of a solution of potassium chlorate containing 70.3 mg. of the pure salt was added to 25 cc. of the potassium iodide solution mentioned above and 50 cc. of fuming hydrochloric acid. After standing fifteen minutes in the stoppered bottle, 5 cc. of chloroform were added and the titration completed. Required: 13.65 cc. of the iodate. As the iodide is equivalent to 31.0 cc., 17.35 cc. correspond to the chlorate, whence 70.9 mg. of potassium chlorate were found. In a second similar experiment only 40 cc. of hydrochloric acid were used, and the mixture was titrated at once, without standing. In this case 13.98 cc. of iodate were required, hence 69.55 mg. of chlorate were found. This shows, as was expected, that the chlorate must be left for some time in contact with the hydrochloric acid and potassium iodide for the completion of the reaction. In a third experiment exactly similar to the last except that the mixture was allowed to stand twenty-four hours before titration, 13.77 cc. of iodate were required, whence 70.41 mg. of chlorate were found.

It is therefore a matter of indifference whether the time of digestion is a quarter of an hour or twenty-four hours. In a fourth experiment, 5 cc. of another potassium chlorate solution containing 33.46 mg. of the pure salt was allowed to stand for ten minutes with 10 cc. of iodide solution and 20 cc. of fuming hydrochloric acid, then 5 cc. of chloroform were added, and the titration was performed. Required: 4.23 cc. of iodate. Calculated for the iodide, 12.40 cc., whence 33.39 mg. of chlorate were found. Other experiments, not necessary to detail, show that there must be a decided excess of iodide as compared with the chlorate; otherwise the results are likely to be a little too low. The necessary working conditions for the titration of a chlorate can be prescribed as follows.

To the solution of the chlorate, add an exactly known amount of pure potassium iodide (a titrated solution may be used), in a glass-stoppered bottle, and an amount of fuming, pure hydrochloric acid at least one-third greater than the volume of the solution. Close the bottle tightly and allow it to stand fifteen minutes after shaking, then add 5 cc. of chloroform. On now shaking, the chloroform must become deep violet. If the color is pale, an insufficiency of iodide has been added, and it is better to begin again rather than to attempt to bring the analysis into order. Now add the decinormal iodate with intermittent violent shaking until the chloroform becomes colorless, which point can be estimated with the utmost precision. Each cubic centimeter of a decinormal iodate solution is equivalent to 2.782 mg. of $(\text{ClO}_3)'$.

Solutions of arsenious acid or chloride can be titrated in the same way as iodides, the reaction being expressed by the equation



In this case, however, unlike the other, a too great concentration of hydrochloric acid must be avoided, since under those conditions the end-point becomes obscure, probably a phenomenon connected with the formation and dissociation of arsenic pentachloride. The suitable concentration of the acid is therefore confined within somewhat narrow limits, but not so narrow as to cause any practical difficulty in working. It was found that 30 per cent. of hydrochloric acid, calculated on the weight of the entire liquid at the close of the titration, exceeds the permissible maximum limit, while 25 per cent. does not. On the other hand, the minimum limit is in

theneighborhood of 12 to 15 per cent. of acid. For the experiments noted below, a solution of sodium arsenite was employed in which the amount of arsenious oxide had been determined by titration with iodine solution in the ordinary way. Taken: 25 cc. arsenious solution (243.8 mg. As_2O_3) and 50 cc. of fuming hydrochloric acid. Required: 24.45 cc. decinormal = 242.1 mg. of arsenious oxide. Taken: 5 cc. arsenious solution, 5 cc. hydrochloric acid, and 10 cc. water. Required: 4.91 cc. of iodate = 48.6 mg. Found: 48.8 mg. by iodine titration. Taken: 20 cc. arsenious solution and 40 cc. hydrochloric acid. Required: 19.69 cc. iodate = 194.9 mg. arsenious oxide. Found: 194.7 mg. by iodine titration. Taken: 15 cc. arsenious solution and 30 cc. hydrochloric acid. Required: 14.79 cc. iodate = 146.4 mg. arsenious oxide. Found: 146.3 mg. by iodine titration.

To summarize: Add to the arsenious solution an amount of fuming hydrochloric acid sufficient to make the hydrochloric acid equal to about 20 per cent. of the entire mixture at the end of the titration, and 5 cc. of chloroform; then run in from a burette as large a proportion as can be judged of the whole amount of decinormal iodate requisite; shake well and continue titrating with the iodate until the chloroform is colorless. Each cubic centimeter of the standard solution corresponds to 9.9 mg. arsenious acid or 7.5 mg. arsenic.

The determination of antimony is precisely like that of arsenic. A solution was prepared of pure recrystallized potassium antimonyl tartrate, containing 31.251 grams per liter. Twenty-five cc. of this were mixed with 30 cc. hydrochloric acid and 20 cc. water, and titrated as usual. 23.62 cc. of the iodate were required, equivalent to 784.6 mg. tartar emetic found as against 781.3 mg. taken. In this determination the amount of hydrochloric acid should have been greater by 15 cc. In the next experiment, 25 cc. of the antimonious solution with 25 cc. of hydrochloric acid required 23.50 cc. of iodate, equivalent to 780.6 mg. of antimony salt found (781.3 taken). Twenty-five cc. antimony solution with 35 cc. fuming hydrochloric acid required 23.54 cc. of iodate, whence is calculated 781.2 mg. potassium antimonyl tartrate.

Since copper does not interfere in the least with the application of the method, it is possible, for example, to titrate the arsenic in Paris green directly without preliminary separation. Thus, 20 cc. of a sodium arsenite solution with 20 cc. of fuming hydro-

chloric acid required 8.95 cc. of iodate; the same, plus 1 gram of copper sulphate, required 9.00 cc. of iodate. For the analysis of Paris green, 0.5 gram of the substance is dissolved in 15 cc. of water and 25 cc. of fuming hydrochloric acid, and directly titrated with 5 cc. of chloroform and the decinormal solution of iodate.

Ferrous salts can be titrated in exactly the same way as iodides. Taken: 2.0874 grams ammonium ferrous sulphate. Required: 26.06 cc. iodate, equivalent to 297.6 mg. iron found, or 14.26 per cent. Theory: 14.25 per cent. Unlike the titration with potassium permanganate, oxalic acid does not interfere with this determination. Taken: 2.0843 grams ammonium ferrous sulphate and 1 gram oxalic acid. Required: 25.95 cc. iodate, equivalent to 296.3 mg. iron, or 14.22 per cent. Ferric salts do not interfere with any of these titrations, nor do bromides to any serious extent, if the amount is small. The end-reaction in the titration of ferrous salts is somewhat slow and, in spite of the satisfactory results of the test analyses, is lacking in the sharpness that distinguishes the other titrations described in this paper. This difficulty appears to be avoided by the addition of a small amount of manganous chloride, but the point requires further examination.

The method which has been described is adapted to the determination of almost all the substances to which Bunsen's process of distillation with potassium iodide and hydrochloric acid is applicable, with at least equal precision, with less expenditure of time and far simpler apparatus. It is furthermore applicable in certain cases in which the Bunsen method is not, as, for example, the titration of arsenic or antimony in the presence of copper and ferric compounds.

CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA, May 5, 1903.

THE PERMANENT PROTECTION OF IRON AND STEEL.¹

BY MAXIMILIAN TOCH.

Received April 14, 1903.

The question of the permanence of modern steel structures, whether the iron and steel used therein is slowly corroding and will in time cause great calamity by the collapse of these structures, has led chemists and engineers to make extensive researches into

¹ Read before the New York Section of the American Chemical Society.

the stability of iron and steel exposed to atmospheric influence. Both exposed and embedded iron are subject to progressive oxidation under certain conditions, and evidence of this is offered in the record of many cases of rusting of girders and "I" beams of railroad and other bridges, while manufacturers of paints have long endeavored to make a coating of material which would prevent corrosion and oxidation.

The success of such coatings depends mostly upon the skill of the workmen and their proper application. A good paint improperly applied is relatively as poor as a paint of lesser merit. Red lead, for instance, is condemned as often as commended and it is probable that those who have commended it have had it properly applied by skilful workmen under favorable conditions, and then had it covered by better paint. At the same time, it may be regarded as an axiom that it is a blunder to apply a corrosive oxide to a material that will corrode. If a paint be in itself a carrier of oxygen, and the iron or steel be subjected to the action of alternate dampness or dryness or of air charged with carbon dioxide, progressive oxidation is sure to take place and the tensile strength of the metal to be materially reduced. Such conditions may readily occur when a beam is placed in a porous wall. Rapid and continuous oxidation takes place, if steel or iron which is partly rusted is covered with red lead and left exposed.

About fifteen years ago a pamphlet was published in Germany intended to prove that this oxidation is due to electrolytic action, and while the quantity of electricity involved has not been measured, nor positive evidence of it adduced, it seems plausible that such a condition may exist. An iron bar bedding in stone, packed with metallic lead at the point where it enters the stone, always rusts rapidly, suggesting electrolytic action. When two pieces of steel come in contact in a building, rapid oxidation occurs at the point of contact, and this is particularly true of bolt-heads and grill foundation work.

If a clean, pure, cement concrete is packed hard against an iron or steel surface, little or no oxidation can take place, especially if free lime has been liberated in the setting of the cement; but violent oxidation can take place if cinder concrete containing iron oxide, other metallic oxides, free chlorine or any trace of a sulphide be used.

Pieces of anchor chains, which have been embedded in concrete



Fig. 1.

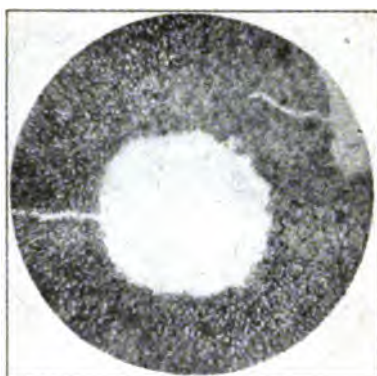


Fig. 2.

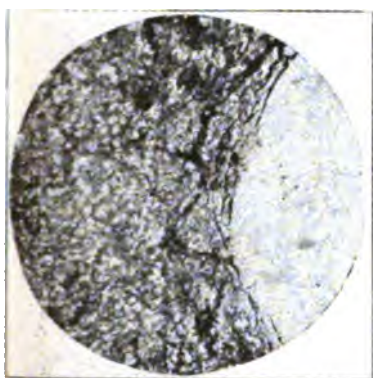


Fig. 3.

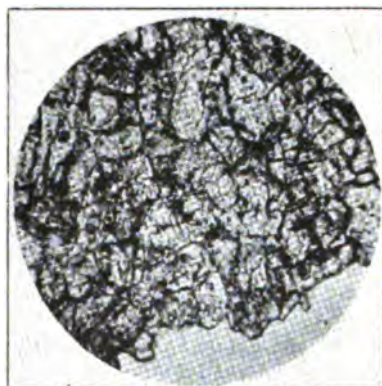


Fig. 4.



Fig. 6.



Fig. 7.

1

2

3

4



Fig. 8.



Fig. 9.



Fig. 10.

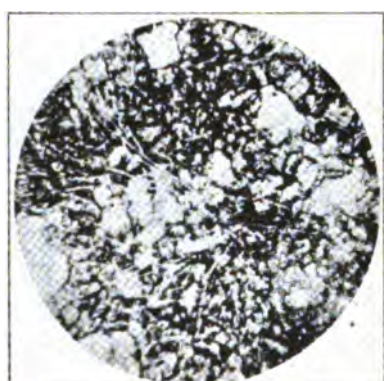


Fig. 11.

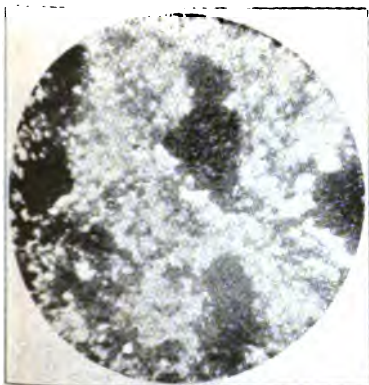


Fig. A.

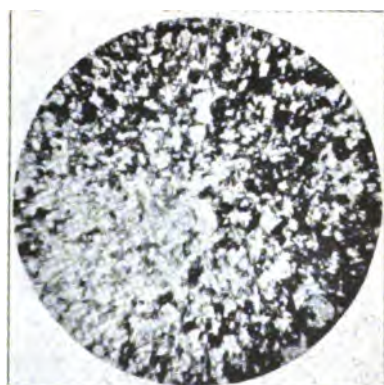


Fig. B.



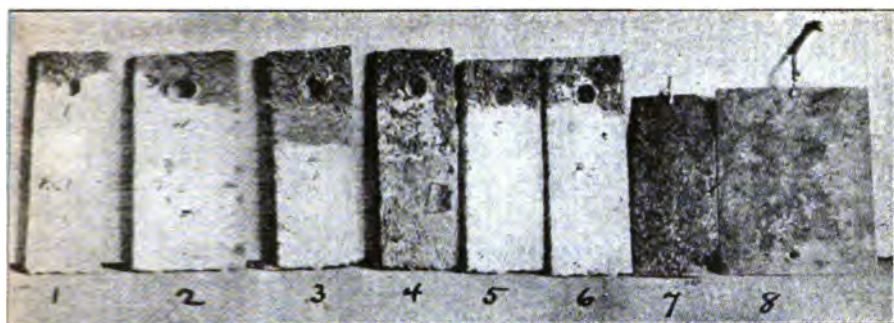


Fig. C.

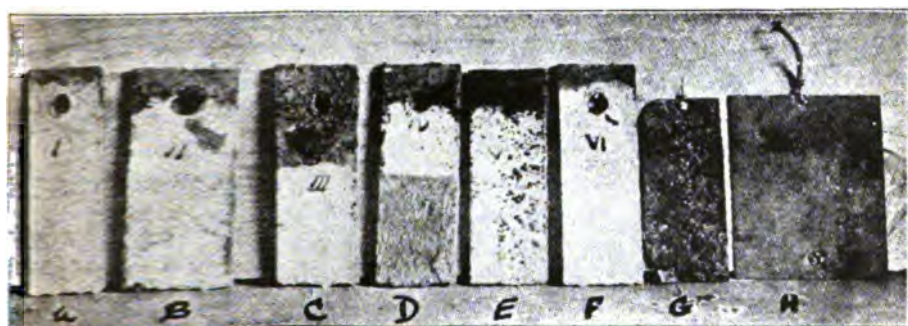


Fig. D.

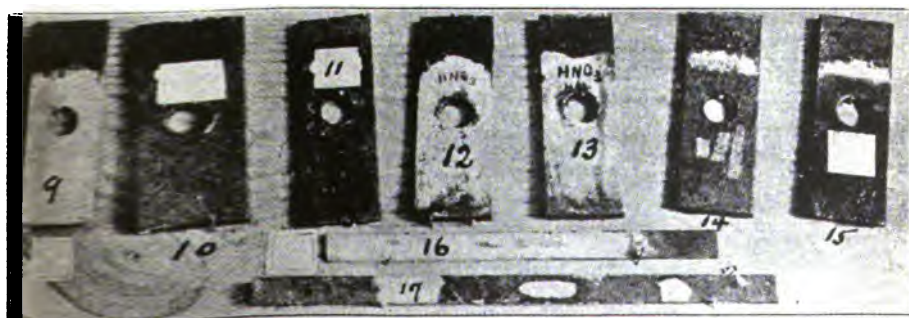


Fig. E.

more than 200 years, have been found in Spain in a state of perfect preservation. Large quantities of metal unearthed in Italy and Greece, extremely old, embedded in cement or concrete, are wonderfully well preserved. These and other observations led me to experiment with Portland cement for the protection of iron and steel against oxidation.

Portland cement, prepared from pure materials in molecular proportions, consists of tricalcium silicate and dicalcium aluminate in a state of solid solution and in the proportion of 85 per cent. of $\text{SiO}_2 \cdot 3\text{CaO}$ and 15 per cent. of $\text{Al}_2\text{O}_3 \cdot 2\text{CaO}$. A Portland cement may also exist in which the aluminate is replaced by dicalcium ferrite, $\text{Fe}_2\text{O}_3 \cdot 2\text{CaO}$. When such a cement is treated with water, it is decomposed, hydration takes place, and hydrated calcium silicate of lower basicity, combined with an alumina or iron compound, is formed and the product is known as *set cement*. Free lime is liberated at the same time and this explains why linseed oil paint applied to newly set cement is ineffective and why a proper mixture of cement over iron precludes oxidation.

I am indebted to Mr. Clifford Richardson for the use of certain thin sections of typical Portland cements and synthetic compounds prepared to illustrate the structure and physical properties of these important substances. I have made photo-micrographs of these sections which have been reproduced in the following illustrations.

In the plates

Fig. 1 represents synthetic $\text{SiO}_2 \cdot 3\text{CaO}$.

Fig. 2, synthetic $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 6\text{CaO}$.

Fig. 3, synthetic $\text{SiO}_2 \cdot 4\text{Al}_2\text{O}_3 \cdot 10\text{CaO}$.

Fig. 4, Universal Portland cement clinker.

Fig. 6, Portland cement clinker containing 7 per cent. Fe_2O_3 and no Al_2O_3 .

Fig. 7, Celite in Portland cement clinker.

Fig. 8, synthetic $2\text{Al}_2\text{O}_3 \cdot 3\text{CaO}$.

Fig. 9, synthetic $\text{SiO}_2 \cdot 2\text{CaO}$.

Fig. 10, tricalcium aluminate, $\text{Al}_2\text{O}_3 \cdot 3\text{CaO}$.

Fig. 11, Felite rods in Portland cement clinker.

Fig. A, properly treated Portland cement, finely ground and which sets quickly, magnified 100.

Fig. B, best commercial Portland cement, magnified 100, not fit for paint protection.

To confirm the value of Portland cement for the protection of iron and steel, I prepared cement having the composition above

indicated, that is, 85 per cent. of tricalcium silicate and 15 per cent. of dicalcium aluminate, in solid solution with each other. This substance, reduced to fine powder, was mixed with water to a thin paste and applied to plates of steel. The coated plates were subjected to various unfavorable influences, tending to cause them to corrode and rust. About 2 in. of one end of each plate was left uncovered, and this space was in every case badly rusted. When the treatment was completed, the plates were all photographed and the photographs reproduced in the following illustrations.

In the illustrations, Figs. C and D, 1 to 6, and A to F, respectively, represent the same set of plates which were submerged in earth through which was passed, for a period of three months, a current of electricity from a crow foot battery of two cells. The earth was moistened alternately with ammonia, weak nitric acid, and an aqueous solution of ammonium chloride and water. The plates were set in a row, parallel with each other. In the illustrations, Fig. C, 1 to 6 represents the anode sides, and Fig. D, A to F, the cathode sides of the plates.

Fig. 7 represents the plate which was connected with the anode wire and 8, that connected with the cathode wire.

Fig. C, 7, and Fig. D, G show that the anode plate was completely rusted even around the edges, while Fig. C, 8 and Fig. D, H show that the anode plates were much better preserved.

In Fig. C, plate No. 1 was properly treated with pure Portland cement. When removed from the ground it was perfectly preserved and showed no trace of oxidation.

Plate No. 2 was treated with commercial Portland cement containing some metallic iron and calcium sulphate. Marked incrustation of rust appeared under the cement.

Plate No. 3 was coated with an oil paint and afterward covered with cement. It was fairly well protected.

Plate No. 4 was first coated with cement and the latter afterward covered with oil paint. The steel was perfectly preserved.

Plates Nos. 5 and 6 were covered respectively with different samples of Portland cement, the covering of No. 5 being worthless and that of No. 6 excellent.

Fig. E, plates numbered 9 to 17, respectively, were coated with various cement and paint preparations, and subjected to the action of different conditions and reagents. The effect in each case is indicated in the illustration.

Plate No. 9 was coated in the same way as plate No. 1 and for three months was sprinkled with water once a week and allowed to dry. The uncoated portion was badly rusted, but the covered portion was perfectly protected.

Plate No. 10 was coated with cement and an oil paint. Plate No. 11 was coated with cement, and a hydrocarbon paint. It was subjected to water and the elements alternately with no unfavorable result.

Plates Nos. 12 and 13 were coated with cement in the same way as plate No. 1 and then supported in a large beaker, the bottom of which was covered with fuming nitric acid. Some of the acid touched the lower end of the plates and lightly corroded them. The uncovered portions were badly corroded, but the acid fumes did not penetrate the cement, and the plates remained in an excellent state of preservation.

Plate No. 13 was subjected for a short time to the influence of fume liberated after addition of hydrochloric acid.

Plate No. 14 was first coated with hydrocarbon oil paint. Subjected during three months to nitric acid fumes, it showed no corrosion under the cement.

Plate No. 15 was prepared in the same way as No. 14 and subjected to the influence of sulphuric acid, carbonic acid and steam; underneath the coating it was thoroughly preserved.

No. 15 is a bar of steel which was coated with a wash of cement of the best commercial grade. The protection was fairly good, but the coating, exposed to wind and rain, was washed off after a few months.

Plate No. 17 was covered first with oil paint and afterward with prepared cement. Roughly handled during eight months, the covering flaked off and the steel was badly corroded.

As a result of the experiments made with the mixture prepared and applied after the manner just described, we may conclude:

(1) If a proper cement paint be applied to a surface which has begun to oxidize, further oxidation will be arrested.

(2) If the cement used be very fine and free from iron, calcium sulphate and sulphides of low specific gravity, it will quickly set on the surface and eventually become thoroughly fixed upon the metal so that rain will not wash it off.

(3) When thoroughly applied, even to three coats, the concrete may be painted with alkali proof and adherent paint, afford-

ing absolute protection to iron so that moisture, carbon dioxide or factory fumes will not penetrate.

(4) Cement paste for application to iron or steel must be made with pure water, and the mixture must be stirred at least fifteen minutes to admit of the liberation of the lime.

(5) Free lime on the surface of the cement coating is quickly carbonated, and then has no injurious action upon linseed oil paint which may, under such conditions, be applied and become extremely efficacious.

The method of waterproofing brick walls from the outside as a protection against penetrating rain or dampness is important in this connection. A newly set brick contains as much as 8 ounces of water, and its power to adhere to the mortar increases with the quantity of water it contains. If a linseed oil paint be applied to a newly erected and wet wall, it quickly peels off and ruins the wall for the further application of paint. But if a proper cement mixture is applied to such a wall in the form of paint or whitewash, it not only adheres perfectly, but forms an excellent base for the application of a good linseed oil paint. Painting the outside wall of a building in this way has some influence on the permanent protection of iron and steel used in construction, since it prevents in a large degree the access of carbonic acid, moisture and gases.

In view of what has just been stated, it is reasonable to believe that structural metal works which have been coated with a layer of cement paint and further protected by a layer of hydrocarbon insulating paint, when embedded in masonry, will be perfectly immune to oxidation and will probably last for all time.

A similar coating affords efficient protection to pipes and conduits placed in the ground and subjected to various influences such as of moist gases, electric currents, acid and alkaline liquids.

Pure Portland cement mixed with water cannot be used as a wash on metal because it will not always set, and it is apt to crack when it does, hence it must be diluted. But care must be exercised that the dilution be not carried too far and the strength of the cement thereby impaired. Voids can be prevented by careful brushing, and for certain structural works where brush work is impracticable, spraying will be effective, but the cement must then be applied in several layers.

NOTES.

Note on the Mononitro-o-Phthalic Acids.—Since the publication in this Journal of the article by Bogert and Boroschek¹ upon the mononitro-*o*-phthalic acids, certain facts have come to light which seem to call for a few additional notes from us.

In the first place, we have discovered, among a number of dissertations recently secured by Columbia University, several dealing wholly or in part with the nitrophthalic acids. Two of these, namely, one by Max Levi, submitted to Freiberg (i. B.) University in 1891, the other by Adolph Koch, submitted to the University of Geissen in 1900, antedated part of the work reported by us. So far as we know these results have not been published in any of the chemical journals and do not appear in "Beilstein." Of the derivatives prepared by us, the following are also described in these dissertations.

3-Nitrophthal-1-Amic Acid.—By the action of hydrochloric acid upon the sodium salt of the imide, Levi² obtained a crystalline compound to which he assigned the 1-amic acid structure. The acid prepared by us by the action of baryta water upon the imide, and for which we suggested the 2-amic acid constitution, has recently been shown by Kahn³ to be the 1-amic acid. As Levi did not analyze his product and gives very few data concerning it, it is doubtful whether he really had the pure 1-amic acid in hand, particularly as he reports the substance to be "quite easily" soluble in ether, whereas the 1-amic acid is really very difficultly soluble in ether.

3-Nitrophthal-1-Anilic Acid.—Levi also reports an anilic acid, crystallizing in white needles, melting-point 232°, which does not at all correspond to the pale yellow needles obtained by us, which melt at 180° with formation of the anil. We thought it likely that this acid had the 2-anilic acid form, but Kahn's work makes it seem much more likely that it possesses the 1-anilic acid structure.

3-Nitrophthalamide.—The amide prepared by Levi melted at 219°, while our product melts at 200°-201° with formation of the imide.

4-Nitrophthalamilic Acid.—The anilic acid prepared by Levi

¹ This Journal, 23, 740-761 (1901).

² Loc. cit.

³ Ber. d. chem. Ges., 35, 3866 (1902).

melted at 204° (uncorr.); our product at 181° with formation of the anil.

4-Nitrophthalimide.—This was prepared by Levi by the action of ammonia upon the anhydride and also by the action of ammonium thiocyanate upon the free acid. His product is apparently the same as that obtained by us subsequently. To the imides of both nitrophthalic acids, Levi assigns the unsymmetrical structure, in the derivatives of the 3-nitro acid placing the imide group ($:NH$) upon the carbon non-adjacent to the nitro group (a formula, by the way, recently supported by Kahn, in a private communication to one of us).

4-Nitrophthalanil.—Prepared by Levi before either Graebe and Bueznod¹ or ourselves.

4-Nitrophthalamide.—Also prepared by Levi before us.

4-Azophthalic Acid.—Koch² obtained an azo acid by the electrolytic reduction of 4-nitrophthalic acid in alkaline solution, and describes the substance as an orange-yellow to rose-red precipitate, decomposing and partly subliming at 200° . We reported two different forms of 4-azophthalic acid: one, by reducing an alkaline solution of 4-nitrophthalic acid with sodium amalgam, was a salmon-colored, crystalline substance not melting below 360° , and giving a silver salt insoluble in hot water; the other, by oxidizing azophthalide with alkaline permanganate solution, separated as a reddish yellow, crystalline precipitate, melting with decomposition at 285° - 300° , and yielding a silver salt partly soluble in hot water. The products of all these methods show about the same solubilities in water, alcohol and ether.

It seems not amiss in this connection also to call attention to the fact that 3-nitrophthalic anhydride was prepared by Leupold³ from the corresponding acid and acetyl chloride three years before Lipschitz⁴ reported the same method for the production of the anhydride.

Kahn has recently criticized our method of preparing this anhydride, stating that, in his experience, six to eight hours' heating of the acid at 235° - 240° causes considerable decomposition. In his first article⁵ he recommends a temperature below 218° , while

¹ *Ber. d. chem. Ges.*, 32, 1992 (1899).

² *Loc. cit.*

³ *Inaugural Dissertation*, Basel, 1897, p. 22.

⁴ *Monatsh. Chem.*, 21, 793 (1900).

⁵ *Ber. d. chem. Ges.*, 35, 472 (1902).

in his second¹ he states that a temperature of 230° is about right. As the temperature reported by us (235°-240°) merely represented the temperature of the heating medium, the reaction being conducted in an open flask in the oil-bath, it is probable that the actual temperature of the melt was not far from 230°. We did not determine the temperature of the melt exactly, since our interest lay more in determining the possibility of obtaining the anhydride by heating the acid than in the question of the exact temperature at which the best yield was secured, in view of the fact that Lipschitz² shortly before had reported that the anhydride could not be satisfactorily prepared in this way. The fact that the acid is liable to decompose when heated too high was, of course, observed by the earliest workers in this field.³ Our product, however, was not overheated and showed no signs of decomposition, the solidified melt being light yellow, crystalline and homogeneous. The duration of the reaction, as reported by us (six to eight hours) represented the time consumed in raising the temperature of the oil-bath very gradually until it reached 235°-240°, when no more water was evolved and the flask was removed from the bath. As Kahn has shown, heating for half an hour at 230° is sufficient to complete the reaction.

Concerning the discovery of 3-nitrophthalic acid, the impression might be gathered from certain reference works (Beilstein, Roscoe-Schorlemmer, *et. al.*, in which the name of Marignac precedes that of Laurent, in giving the earliest literature upon the subject, that the work of the former anticipated that of the latter. As a matter of fact, Laurent's work antedated Marignac's by at least a year, as appears from the following: Laurent, in studying the action of nitric acid upon naphthalene, isolated, among other products, an acid which he called "nitrophthalic," and prepared its anhydride, acid ammonium salt and imide. These results were sent to the French Academy of Sciences, on March 16, 1840.⁴ By a strange mischance, not only this memoir but four others by the same author upon new compounds of naphthalene were mislaid in the office of the latter journal and lost. When Laurent learned of this loss, he immediately requested De Quesneville to

¹ *Ber. d. chem. Ges.*, 35, 389 (1902).

Loc. cit.

² Laurent: *Compt. rend.*, 12, 1193; Marignac: *Ann. Chem.* (Liebig), 38, 9; Laurent: *Rev. scientif. Indus.*, 6, 95 and 12, 602; de Aguiar: *Ber. d. chem. Ges.*, 8, 899; Kronberg: *Inaugural Dissertation*, Göttingen, 1881, p. 32, etc.

⁴ *Rev. scientif. Indus.*, 8, 363; 6, 76-77.

copy the duplicates which had been deposited with the secretary of the Academy and to publish the same in the *Revue scientifique et Industrielle*. This was done, the article appearing four or five months later in Vol. 6, pp. 76-99. Laurent also reported his work upon nitrophthalic acid at the meeting of the Academy, June 21, 1841.¹ Before the publication of Laurent's delayed article in the *Revue scientifique et Industrielle*, a paper appeared in Liebig's *Annalen* (38, 1-13) by Marignac of Geneva, likewise dealing with the action of nitric acid upon naphthalene and announcing the discovery of "nitronaphthalic acid" (identical with Laurent's "nitrophthalic acid") and the preparation of some of its salts. Later in the same year (1841), Laurent² called attention to the fact that his work had anticipated Marignac's by at least a year.³ and so far as we are aware, this claim was never disputed by Marignac. It seems, therefore, that the major portion of the credit for the discovery of nitrophthalic acid belongs to Laurent, not alone because he was actually the first to obtain the acid, but also because Marignac (as he himself acknowledges—*Loc. cit.*) was only following in a line of investigation already largely worked out by Laurent. M. T. BOGERT AND L. BOROSCHEK.

ORGANIC LABORATORY, COLUMBIA UNIVERSITY,
May 14, 1903.

A Cheap and Efficient Water-blast.—The work performed in the chemical laboratory of Cornell College emphasized the necessity of a water-blast, and some of the well-known kinds were purchased. The laboratory is situated on the third floor of the building where the water pressure was found to be scarcely 30 pounds to the square inch. This was not sufficient to maintain the blasts satisfactorily. It was therefore necessary to set about to devise a blast which would be suitable where the water pressure is low and which would give good results with a small jet of water. The apparatus here described has been in use for about four months and seems fully to meet the conditions.

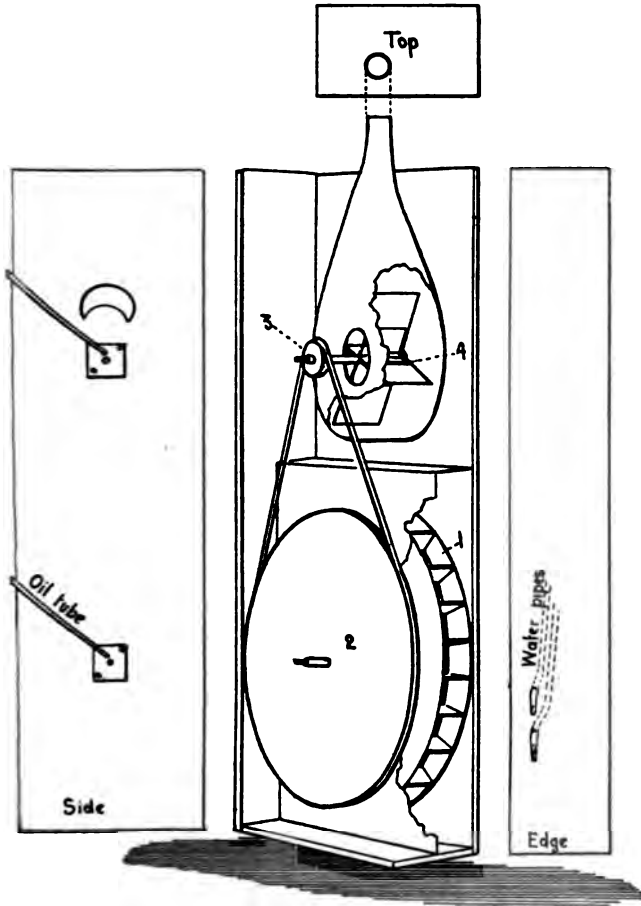
Experiments with various devices were made, but the one that has given the most satisfactory results consists of a small water-wheel (1), a large pulley-wheel (2) connected by belt with a small one (3) for driving a fan wheel (4), all of which are enclosed in a rectangular wooden box 7 x 12 x 24 inches.

¹ *Compt. rend.*, 12, 1193.

² *Rev. scientif. Indus.*, 9, 31.

³ *Ibid.*, 8, 363-364.

The water-wheel is 9.5 inches in diameter, and 1.5 inches thick and is made of galvanized iron. Its construction is something on the plan of an undershot wheel. There are twelve paddles on the rim, projecting an inch, against which the water strikes to produce the motion. Each paddle is placed in line with a radius



of the wheel. The larger pulley-wheel has a diameter of 10 inches, is of a good quality of white pine and was soaked for three hours in melted paraffin to prevent warping. It has a groove $\frac{3}{8}$ of an inch for the belt. These wheels are mounted on a $\frac{3}{8}$ inch shaft, turned down at each extremity to $\frac{1}{8}$ inch bearing. The smaller pulley-wheel is of wood $\frac{3}{4}$ of an inch in diameter, with flanges

$\frac{1}{4}$ of an inch deep. The fan-wheel consists of four wooden paddles and is 6 inches in diameter. This wheel and the smaller pulley are mounted on a $\frac{3}{8}$ inch shaft which is likewise turned down to $\frac{1}{8}$ inch journals. The boxings in which the journals run are simply pieces of iron $\frac{1}{8}$ of an inch in thickness, with holes drilled to fit the journals, and the iron pieces are fastened to the inside of the case. The water-wheel is separated from the rest of the apparatus by an air-tight tin partition to confine the water, which is conveyed to this wheel by two tubes consisting of mouth-blowpipes cut off at the small extremity to attain an inside diameter of $\frac{3}{32}$ of an inch. These are placed through the edge of the case in such a way that the water from one strikes the paddles just a little below the axis at an angle of 45° to the horizontal plane of this axis, and from the other lower down and nearly parallel to this plane. The best effect is attained when the stream strikes the center of the paddle, when the paddle is exactly at a right angle with the stream. Ordinarily it has been found necessary to employ only one stream of water. Ample provision must be made for the escape of the waste water.

The fan is enclosed in a galvanized iron compartment, and is somewhat like the fan used by the blacksmith. It should have an outlet air tube with an inside diameter of $\frac{1}{2}$ inch. By attaching a Y-tube to this, two blasts can be used as easily as one. A thick-walled rubber tube, about $\frac{1}{4}$ of an inch in diameter has been found to be the most efficient belt. The bearings must obviously be kept well lubricated to secure easy action.

CHEMICAL LABORATORY, CORNELL
COLLEGE, May 8, 1903.

FRANK L. HANN.

Rapid Determination of Phosphorus in Steel.—If the yellow precipitate, obtained from 1 gram of drillings, as usual, by shaking in an Erlenmeyer flask, be transferred together with the liquid to a 7-inch test-tube and, after standing one-half hour (a highly essential precaution), be whirled in a centrifugal machine, the supernatant liquid may be poured away and the last drops drained off without any danger of any of the precipitate being carried with it. This is a fact of considerable practical importance as it enables us to dispense with the filtration and prolonged washing which are the most tedious and laborious part of the Handy method. The liquid still adhering to the precipitate and walls of the test-tube after the first decantation and draining, amounts to an error of

about 0.12 per cent. of phosphorus according to Handy's method. But if the test-tube be then nearly filled with water, stoppered and the contents well mixed, again whirled, and the liquid again poured and drained off, the error is reduced to less than 0.001 per cent. The precipitate is then dissolved in standard alkali, and titrated with standard acid as in Handy's method. The Götz method, on account of its inexactness, seems to find but little use. For the method here described, 1 gram of steel is dissolved in 50 cc. of nitric acid (sp. gr. 1.135), the solution boiled, a little solid permanganate added, again boiled, decolorized with sugar or ferrous sulphate, cooled, 10 cc. of strong ammonia and 50 cc. of molybdate solution added, and the mixture shaken as usual in an Erlenmeyer flask.

GEORGE AUCHY.

NEW BOOKS.

ELEMENTARY CHEMISTRY. BY ROBERT HART BRADBURY, A.M., PH.D.,
Teacher of Chemistry, Central Manual Training School. Phila., etc.
New York: D. Appleton and Company, 1903. Price, \$1.25.

The author offers this volume for the use of students in colleges and secondary schools. It consists of two parts—a descriptive portion of 328 pages, and a second part of 157 pages, devoted to the experimental work.

The book is well written and presents its facts clearly and accurately.

The arrangement is that which this particular teacher has found productive of the best results with the students in his charge.

"The theoretical portion is interwoven with the descriptive matter No generalization is presented until after a particular case of it has been carefully described More stress is laid upon the mechanism of chemical changes . . . than upon particular facts It is far more important that the student should understand the behavior of crystal hydrates in general . . . than that he should memorize the number of molecular weights of water in the formulas of innumerable salts."

The author acknowledges his great indebtedness to Ostwald's publications and to the influence upon him of the school of which this scholar is the leading exponent.

The book is well printed and illustrated, containing portraits of Moissan, Priestley, Davy, Rutherford, Lavoisier, Dalton, Wöhler, Liebig, Bunsen and Mendelejeff. It will prove interesting to every teacher of the science and particularly to those who train beginners.

EDGAR F. SMITH.

A TEXT-BOOK OF ORGANIC CHEMISTRY. BY WILLIAM A. NOYES, Professor of Chemistry in the Rose Polytechnic Institute. New York : Henry Holt & Co. 1903. 534 pp. Price, \$1.50.

Among the short text-books of organic chemistry, this appears as a refreshing innovation. Of the extent of but 534 12mo. pages, it manages to compass the relationships of carbon compounds remarkably well. This is done by masterly grouping, and by a prudent distribution of stimulating reading matter. The style of statement is clear, direct and somewhat less technical than the prevalent language of organic chemistry, but the subject is often carried beyond the range of a beginning student of carbon compounds. Some parts of the book seem best adapted to the understanding of those who have already made things in the organic laboratory or have otherwise found their own way in the labyrinth of carbon combination. The question of its use in lectures not preceded by the student's laboratory work is one to be settled by the teacher in actual trial.

Without doubt the book is made the more clear and simple to any learner in that he is given the full benefit of the latest conclusions of research. Every part is freshly written in the light of the present. As instances may be mentioned, the explanation of alcohol and phenol reactions as those of hydroxides on pages 128, 143 and 283; the definition of acids on page 221; the possible structure of crystallized oxalic acid on page 250; esterification in general on pages 279-282; ethers compared with hydroxyl compounds as to their boiling-points on page 284; isocyanide structure on page 305; compounds of a single carbon atom on page 313; the reactivity of halogen compounds of carbon on page 390; the "strength" of organic bases on page 424.

In the division of subject-matter, the hydrocarbons, both aliphatic and aromatic, are brought first into 65 pages, then alcohols with phenols and their ethers are given 44 pages, the aldehydes, ketones and quinones 48 pages, the acids, aliphatic and aromatic, 52 pages. Nitrogen compounds have their more distinct introduc-

tion among the derivatives of the acids. The hydroxy and ketonic acids in 43 pages are followed by the carbohydrates in 22 pages. The descriptive chemistry of halogen compounds is very briefly given, still later.

The work is eminent throughout for its comparative presentation of corresponding reactions and structures, including those seldom grouped together. It is in this way that the attempt modestly acknowledged first in the preface is measurably realized "to present the fundamental facts of organic chemistry for the use of those beginning the subject." But it is in the consolidation of aliphatic and aromatic chemistry that, as said in the preface, "the most radical departure" of the author is made, in the adoption of what appears to him "a more fundamental and logical classification."

That the binary division of carbon chemistry, in use for about thirty years, is suffering numerous complications may be noted by glancing through the outline of ring systems, as in M. M. Richter's "Lexicon," or by a survey of any such class as the terpenes. Many of us who teach have for some time been compelled to present evidence of closed chain structure along with that of open chains, that the student's mind may have the benefit of contrasts and relationships from the first. And it is always a question, how many parallel relations can be carried together with advantage in a given teaching method.

The question has been less serious, when it has been asked, shall the poly-derivatives be all taken along with those of monovalence through the round of oxygen and halogen and nitrogen union, or shall the mono-derivatives be first taken carefully through the stages by themselves? Now the graver question is before us, shall we study together the like derivatives of all the leading orders of hydrocarbons, comparing them all with each other first as hydroxyl compounds, before entering upon their ethers, and so on? Whatever the answer may be in the interest of logical arrangement, to be adopted in handbooks, or in the compilation of abstracts, the teacher will find the necessity of repetition. In organic chemistry the arrangement of matter in the text is seldom found to be just the best consecutive order for presentation in class-work, and this the teacher must decide upon for himself.

As a compact system of the relationships of carbon compounds, having regard to those of greatest interest, within the compass of a

primary text, this work appears to the present writer to be a very valuable contribution. The consolidation of the aliphatic and aromatic divisions is an experiment in the literature well deserving to be made, and we owe thanks to the author.

The tabulation of derivatives is such as to be suggestive to the teacher and convenient for the learner. Much of it is unique, as that of aldehydes and ketones at page 170. At the close of each chapter is a list of the related laboratory exercises. The introductory chapters upon purification, analysis, and molecular weights, and upon the various physical determinations are excellent.

A. B. PRESCOTT.

NOTES ON METALLURGICAL ANALYSIS. BY NATHANIEL WRIGHT LORD, E.M. Second edition rewritten and greatly enlarged. Metallurgical Laboratory, Ohio State University, Columbus, Ohio. Price, \$2.50.

The first edition of this work was written for the use of the students in the Ohio State University, and the second edition has been enlarged to a manual covering the greater part of the methods in use in steel works laboratories. Besides the analysis of iron and steel, it contains a chapter on sampling and short descriptions of methods for the assay of copper and zinc ores.

The descriptions of the methods chosen are, as a rule, clear and in sufficient detail, and references are given in many instances to the original papers, which will prove valuable where reference libraries are within reach.

There is no index and as the running head-lines consist of the title of the book, reference to the subject-matter is difficult. There are comparatively few illustrations, and the appearance of the book is poor and lacking in finish.

ANDREW A. BLAIR.

QUANTITATIVE CHEMICAL ANALYSIS BY ELECTROLYSIS. BY PROF. ALEXANDER CLASSEN, PH.D., Privy Councillor, Director of the Laboratory of Electrochemistry and Inorganic Chemistry in the Royal Institute of Technology at Aachen. Authorized translation, fourth English from the fourth German edition, revised and enlarged, by BERTRAM B. BOLTWOOD, PH.D., formerly Instructor in Physical and Analytical Chemistry in the Sheffield Scientific School of Yale University. New York: John Wiley and Sons. 1903. 8vo. vii + 315 pp. 102 illustrations. Price, \$3.00.

The name of Professor Classen is so indissolubly connected with the development of electrochemical analysis, and the earlier editions of this book are so favorably known that the present one

is sure of a warm welcome, the more so as it is not merely a translation but a thorough revision which places at the command of English readers the more important results which appeared in Classen's *Ausgewählte Methoden der Analytischen Chemie* (1902), as well as in recent publications by other authors.

The first part, comprising half the book, is devoted to the presentation of the theory and to a description of apparatus and laboratory arrangements. The treatment of the theory is brief (54 pp.), goes directly to the point and is as clear as so condensed a statement can be made. The necessary apparatus is very fully and completely described with the aid of a liberal number of illustrations. The description of the electrical installation of the laboratory at Aix contains many suggestions likely to prove of interest and value to those concerned in introducing new equipment for similar laboratories in this country.

The second part of the book treats of the determination and separation of the metals and halogens. In connection with each topic, references to the literature are given, which, while by no means exhaustive, are sufficiently full for practical purposes. A series of examples are brought together showing the mode of applying electrochemical methods to the analysis of a considerable number of alloys, copper ores, cinnabar, molybdenite, etc.

The labor of the translator is excellently well done, no trace of the German original appearing in the style. A slip, which may be a mere printer's error, occurs in the foot-note on page 281, where "the practical value *in* these examples" is referred to, the author doubtless intending to say *of*. Another typographical error, of which there are not many, is to be found on page 4, where the name of J. B. Hannay is printed *Haunay*. A full index, separated after the German fashion into authors and subject, concludes the book, which is one that can not well be dispensed with in any analytical laboratory.

LAUNCELOT W. ANDREWS.

PHYSICAL CHEMISTRY FOR PHYSICIANS AND BIOLOGISTS. BY DR. ERNST COHEN, Professor of General and Inorganic Chemistry in the University of Utrecht. Authorized translation from the German by MARTIN H. FISCHER, M.D., Instructor on Physiology in the University of California. New York: Henry Holt & Co. 1903. 343 pp.

The book consists essentially of seventeen lectures delivered by Professor Cohen in Amsterdam before a gathering of physicians. The original German edition appeared in 1901 from the press of

Wilhelm Engelmann, Leipzig, and has met with universal favor both at home and abroad.

According to the author: "These lectures are in no way a text-book of physical chemistry." He says further: "I have merely endeavored to show in them the close relation that exists between this new branch of chemistry and the biological sciences, and also, in response to the wishes of my hearers, to describe in some detail the more important methods of physical chemistry."

The treatise does, however, come fully as near satisfying the requirements of such a text-book as do a number of the more pretentious volumes at present available, and may be heartily recommended to a much wider class of readers than is indicated in its title. The theoretical treatment throughout is as rigorous as can fairly be expected in a book of its scope. The author has made free use of the nomenclature of the calculus in the lectures on reaction velocity but the verbal explanations accompanying the formulas make clear in concrete form, the gist of the mathematical processes without burdening the reader with the details of their derivation, and should serve to rob such symbols, when met with in the larger texts or current literature, of much of the mystical element which they too often possess in the eyes of the chemist and biologist. Sufficient of laboratory detail has been introduced to give a strongly objective background to the theoretical part.

The subjects treated in the individual lectures are respectively: 1, Reaction velocity; 2, the inversion of cane-sugar and catalyses in general; 3, the action of ferments; 4, the influence of temperature upon reaction velocity; 5, 6, and 7, equilibrium; 8, the friction of liquids; 9, osmotic pressure; 10, the determination of molecular weight of dissolved substances; 11 and 12, the theory of electrolytic dissociation; 13, 14, and 15, applications; 16, electromotive force; 17, the theory of galvanic elements.

The scope of the applications may be judged from the sub-heads of 13 to 15 which are: The field of hygiene; disinfection in the light of the theory of electrolytic dissociation; the field of pharmacology; the field of physiology; the osmotic pressure of animal fluids; the osmotic pressure between mother and child; osmotic analysis; poisonous effects. The translator has done his work well, preserving both the form and spirit of the original without unpleasantly warping the English.

It is certainly gratifying to see with what readiness the medical

profession and the general biologist are adopting the methods and results of physico-chemical inquiry. The time seems to have really arrived when it is as necessary to point out the present limitations and tentative character of our methods and conclusions as to urge their more rapid extension to wider fields. The outsider who dips into physical chemistry for cut-and-dried methods to solve his own problems is dangerously apt to carry off a mere shell of formulas without realizing how highly specialized are the "simplifying conditions" upon which they are based. It is far too easy to overlook with what care the particular illustrations in our standard texts have been selected. The physico-chemical problems of biology and medicine are for the most part of a far more complicated character than any as yet systematically investigated in pure chemistry, and we must not be too easily satisfied with superficial analogies. It seems to be a trait of human nature to place most confidence in the results of those studies of which we know the least. Professor Cohen's book should certainly do much toward correcting this tendency in the field with which it deals. There seems at present a great need for just such border-line treatises as the book before us and particularly for those of perhaps even a more pointedly conservative standpoint. The impetus to the new movement has been well given; what it most needs now is careful guidance.

F. G. COTTRELL.

TRAITÉ DE CHIMIE PHYSIQUE. LES PRINCIPES. BY JEAN PERRIN.
Paris: Librairie Gauthier-Villars. Price, 15 francs.

M. Perrin's book is not by any means what the chemist would expect to find under such a title. Its guiding idea is better suggested by the opening phrase of the preface: "I have gathered together in this first volume the principles whose study and discussion seem to me to form a natural introduction to the different physical sciences." It is not surprising, then, to find that the first half of the book is really a treatise on mechanics and heat, made up largely of what we are accustomed to call mathematical physics, with here and there a paragraph on the chemical aspects of the matter in hand.

As suggested by the quotation above, the author promises more to follow. But he warns us against concluding that the succeeding volumes will be as abstract as the present one. The second is to treat of the application of the phase rule to pure substances and to

mixtures; also of the relations between composition and chemical properties. A further part will include the laws of "diluted matter," in the form of gas, or in solution; also electrochemistry. And a final part will treat of colloidal solutions and the chemical action of radiations.

Judging from the present volume, the work when completed will be one of great interest; for, although in the part before us there is a good deal which for the chemist can only be regarded as good discipline, there are also, here and there, many passages which are suggestive and stimulating; none the less so for the fact that the author's reasoning does not always carry conviction with it. Such is, for instance, that in which an attempt is made to give a more imaginable form to the idea of changes of entropy (Chapter V); and that in which the ordinary idea of forms of energy is discussed (Chapter IV).

The contents of the present volume will be sufficiently indicated by giving the headings of the nine chapters which compose it: I, The notion of force; II, The factors of action; III, The principle of equivalence and the notion of energy; IV, Rôle of the factors of action in the production of changes; V, The principle of evolution; VI, Characteristics of stable equilibrium; VII, Pure substances and laws of combination; VIII, Chemical potential; IX, The phase rule. It will be seen that the later chapters have a much more chemical complexion than the earlier ones; nevertheless the treatment throughout is abstract and mathematical, and will not appeal at all to those chemists to whom the calculus is a stumbling-block. To others this work will hardly fail to be interesting.

A. P. SAUNDERS.

DETERMINATION OF RADICALS IN CARBON COMPOUNDS. BY H. MEYER.

Authorized translation by J. BISHOP TINGLE. Second edition rewritten.

New York: John Wiley and Sons. London: Chapman and Hall.

xii + 162 pp. 12mo. Cloth. Price, \$1.00.

The first edition of this little book was reviewed in this Journal, 22, 50, and is already favorably known to organic chemists. The present edition contains over 20 per cent. of new matter, including several cuts. The author has cooperated with the translator in the work of revision.

S. P. MULLIKEN.

LOIS GÉNÉRALES DE L'ACTION DES DIASTASES. PAR VICTOR HENRI.

Paris: Published by Librairie Scientifique, A. Hermann.

This is a well-printed book of 129 pages devoted to a discussion of the general laws of the action of the diastases.

In the study of the general phenomena of the life of organisms, two groups of theories have been proposed. The theories of the first group regard the vital manifestations as being due to physical and chemical actions only. The theories of the other group admit the existence of forces or energies extra-chemical, so-called vital forces. Since all experimental work with organisms of this kind must be based on physical and chemical principles there is no possibility of demonstrating, by experiment, the value of the theories of the second group. It is self-evident that any so-called vital force is beyond the power of experimental research. The work of Mr. Henri, of course, is based upon the assumption that the theories of the first group are the true ones, and he undertakes the study of the general laws of diastatic actions in their chemical and physical relations. The work is confined to the discussion of three diastases only, namely, invertine, emulsine and amylase. These three diastases have the advantage of lending themselves to experimental study more easily than the other members of the group. While the work is confined almost exclusively to the study of the influence of temperature upon diastatic action it seems possible to base upon it a general theory of diastatic action completely in harmony with the laws of general chemistry.

The work consists of an introduction of twenty-five pages, giving the state of our actual knowledge of catalytic action. The first chapter, eighteen pages, is a historical résumé of the laws of the action of diastases. The second chapter, thirty-three pages, is devoted to the experimental study of invertine. The third chapter, thirteen pages, is devoted to a discussion of the theory of the action of invertine. The fourth chapter, six pages, is devoted to the study of the action of emulsine. The fifth chapter, ten pages, is devoted to the study of the action of amylase upon starch.

The chemical reactions which take place under the influence of these ferments are discussed mathematically and chemically, and this discussion will be a great help to those chemists who desire to apply mathematical formula to chemical processes. The study of catalytic action shows that there are various forms of activity, namely: first, catalysis produced by the simple presence of the ferment; second, autocatalysis; third, formation of intermediate combinations which are produced very rapidly; fourth, intermediate combinations which are produced slowly; fifth, the action of the catalyzing agent upon a series of successive reactions.

In the development of the third class of reactions mentioned above, the theory of E. Fisher is cited. It shows that there is a constant relation existing between the diastase and the chemical constitution of the bodies which are transformed by it. Fisher's theory also holds that, for instance, in the inversion of cane-sugar, there is an actual chemical compound at first formed between the ferment and the sugar, and by the subsequent breaking up of this compound there are formed the invert sugar on the one hand, while the diastase is regenerated on the other. This little work will undoubtedly be of great interest and benefit to those who are pursuing the study of catalytic reactions from theoretical and mathematical points of view.

H. W. WILEY.

THE PRINCIPLES OF ANIMAL NUTRITION, WITH SPECIAL REFERENCE TO THE NUTRITION OF FARM ANIMALS. BY HENRY PRENTISS ARMSBY, PH.D., Director of the Pennsylvania State College Agricultural Experiment Station; Expert in Animal Nutrition, United States Department of Agriculture. New York: John Wiley and Sons. 1903. Cloth. 614 pp. Price, \$4.00.

The scope of this very readable work is much broader than the second part of the title might suggest to the casual reader, since the various discussions in it apply in most cases to man as well as to the lower animals. From the preface it appears that the substance of the book was first presented to the public as a course of lectures delivered at the Graduate Summer School of Agriculture in Columbus, Ohio, in 1902; in its present expanded form it covers the whole subject in a more systematic manner than would be possible in a course of lectures and is especially characterized by very full references to the original literature.

The general subject is presented under two heads which lead to a division of the book into two parts: 1, The income and expenditure of matter; 2, the income and expenditure of energy. In Part I, which is largely chemical, there are found very clear descriptions of the early experiments of Liebig, Pettenkofer, C. Voit and other pioneer investigators in this field, and also the recent and more exact studies of the modern workers. Chapter V, 92 pages, of this part of the book deals with the question of the relations of metabolism to the food supply and it would not be easy to find a more intelligible or concise presentation of a subject on which the literature has grown to be enormous. This chapter will prove of value to the physiologist or physiological chemist for general

orientation, and through the foot-notes and literature references will serve as a guide for fuller study.

In Part II we find first a short general chapter discussing the relations of force and energy in the animal body and then a chapter on methods of investigating the liberation and transfer of energy. Although necessarily much condensed, this chapter gives a good idea of the construction and use of combustion and respiration calorimeters with discussion of methods of calculation of results. The modern devices of Atwater and others are described fully enough for the needs of the physiologist or general student. Following this chapter on methods there is a short one on the conservation of energy in the animal body and finally four longer chapters on these topics: "The Food as a Source of Energy—Metabolizable Energy"; "Internal Work"; "Net Available Energy—Maintenance"; "The Utilization of Energy". These are well-written and valuable chapters, and while the contents is largely compilation (it could not be otherwise when the magnitude and nature of the topic are considered) the presentation is such as to show the author's full acquaintance with the field and command of the subject. While most of the illustrations in this part of the work are drawn from experiments upon animals, it is clear that the results reached obtain just as certainly for man. The book may therefore be recommended to the attention of those working outside the domain of agricultural chemistry; it must be recognized as a valuable contribution to the literature of physiological chemistry.

J. H. LONG.

TECHNICAL MYCOLOGY : THE UTILIZATION OF MICRO-ORGANISMS IN THE ARTS AND MANUFACTURES. BY DR. FRANZ LAFAR. Translated from the German by CHARLES T. C. SALTER. Vol. II, Part I. Enmycetic Fermentation. London : Charles Griffin and Co. Philadelphia : J. B. Lippincott and Co. 1903. 189 pp.

The first volume of this well-known work appeared in 1898 and was concerned with a discussion of schizomycetic fermentation, or the fermentations and similar changes produced by fusion fungi or bacteria. In the present book, we have the first part of volume second which treats of enmycetic fermentation, or fermentation by the higher fungi, using the term fermentation in the older sense. The book is divided into three sections (Sections X, XI and XII of the whole work). The first treats of the general morphology and biology of the enmycetes; the second of fermentations by species

of the *mucor* family, while the third deals with fermentations by yeast proper.

This last section contains three interesting chapters and is evidently but the introduction to a full discussion of alcoholic fermentation in general, to appear in a later portion of the work. The scope of these chapters is suggested by their titles: Morphology and Life History of Yeasts; The Anatomy of the Yeast Cell; Chemistry of the Yeast Cell. The completed second volume will doubtless prove as useful to chemists interested in fermentation industries as was the first. The mechanical work on the book is excellent.

J. H. LONG.

THE AMERICAN YEAR-BOOK OF MEDICINE AND SURGERY. Vol. I. GENERAL MEDICINE. Philadelphia: W. B. Saunders and Co. 1903. 691 pp. Cloth, \$3.00 net. Half-morocco, \$3.75 net.

This is a valuable annual publication which has already been noticed in this Journal in a review of the volume issued in 1902. The work has not as wide a scope as the *Jahresbericht für Chemie* and the reviews it furnishes are often critical to some degree. But it furnishes an excellent survey of all that is really important in medical literature from the whole world and in readable form. The rapidly increasing importance of chemistry and chemical physiology in general medicine is shown especially in this last volume, which can be recommended to all who are interested in the scientific side of medical progress. The work is issued in two volumes under the editorial control of Dr. George M. Gould. Volume I is always devoted to medicine and Volume II to surgery.

J. H. LONG.

RÉFLEXIONS SUR LA PUISSANCE MOTRICE DU FEU, ET SUR LES MACHINES PROPRES À DÉVELOPPER CETTE PUISSANCE. BY SADI CARNOT. (Réimpression fac-similé conforme à l'édition originale de 1824.) Paris: A. Hermann. 118 pp. 1903.

This reproduction, evidently photographic, of the classic which founded the science of thermodynamics, is a welcome addition to available scientific literature. The original is rarely to be found; and no ordinary reprint, however finely executed, can quite fill its place. One wonders that the photographic method is not more often used for this purpose, for letterpress which has been proof-read by the author has a virtue which no recomposition can attain.¹ The value of this edition is enhanced by an

¹ Ostwald testifies that the present fac-simile is precise, having compared it with his original copy. (*Ztschr. phys. Chem.*, 43, 640, May, 1903)

appended facsimile of the page of Carnot's note-book in which his prescience of the mechanical theory and equivalent of heat is recorded, and also by the letter of his brother Senator Carnot to the Academy. These are taken from the French edition of 1878. When following once more, in their original dress, the thoughts of the great pioneer, the reader cannot but wonder concerning the marvels which he might have wrought if his life had ended less prematurely.

T. W. R.

INDIA RUBBER AND GUTTA PERCHA, translated from the French of SEALIGMANN, LAMY TORRILHON, AND FALCONNET BY JOHN GEDDES MCINTOSH. London : Scott, Greenwood, and Co. 1903. New York : D. Van Nostrand and Co. Price, \$7.50 net.

After an interval of some years in which no comprehensive work on this subject has appeared, two quite elaborate works have appeared almost simultaneously; the one of which the title is given above, and the work of Dr. Carl Otto Weber on "The Chemistry of India Rubber," published this year by Chas Griffin & Co., London, and J. B. Lippincott Co., Philadelphia. The book before us is the more comprehensive in its scope, covering both the subjects India rubber and gutta percha and, as the subtitle states, in their historical, botanical, arboricultural, mechanical, chemical and electrical aspects. As the translator states in his preface, it has been produced by the collaboration of a well-known technical chemist, an equally well-known India rubber manufacturer, and an expert mechanical engineer with special experience of India rubber and gutta percha plant and machinery. Because of this comprehensive plan, the book is a valuable one for those desiring information on the general subject and its different bearings.

The chemistry of the book is not, however, a connected whole written from the standpoint of our present knowledge of the subject, but is in part quite old and somewhat disconnected. As an example we may note the account of dambonite and dambose, the sugar-like body obtained from galoon rubber by Girard. The authors and the translator have preserved the old notation $C_6H_6O_6$ for the sugar and C_2H_5I for methyl iodide, and the only intimation the reader has that these formulas are not to be taken as written is a brief foot-note of the translator to the effect that "all the formulas and equations given by Girard are evidently old notation." We do not think that there is any excuse for

presenting the matter in this shape by a translator who wishes to make the book as thoroughly available as possible. Again, the word hydrocarbide used all through for the English word hydrocarbon is objectionable and is evidently too close a translation of the French "hydrocarbure." Similar inelegant translation is seen in the use of the word "expiry" instead of "expiration" on p. 97.

Much of the chemical discussion is a reproduction of the views of the original writer given in the first person singular and then with a word of comment, sometimes expressing doubt or dissent, as in the reference of Fawsitt's experiments on vulcanization on p. 137.

The section on the analysis of rubber and rubber substitutes is fairly complete, but is largely given as a quotation from other sources as in the statement of Henrique's contribution.

Taken altogether, the chemical part of the section on India rubber is not as satisfactory in its treatment as that found in Weber's work. The illustrations of this section are also distinctly inferior and many of them so blurred as to make details undistinguishable.

The section on gutta percha is quite complete in the descriptive and botanical parts, but the chemistry of the subject is not as well presented as we find in Obach's fine monograph, which appeared a few years ago in German.

The book conveys a great deal of information but, as shown above, does not seem to present the chemistry of this most interesting subject as well as it might have been done.

SAM'L P. SADTLER.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON THE MOLECULAR REARRANGEMENT OF UNSYMMETRICAL ACYLAMIDINES INTO ISOMERIC SYMMETRICAL DERIVATIVES.

BY HENRY L. WHEELER, TRENT B. JOHNSON, AND DAVID F. MCFARLAND.

In papers from this laboratory, which were published several years ago,¹ it was shown that thioncarbamic esters undergo a molecular rearrangement into thiolcarbamic esters when heated with alkyl halides.



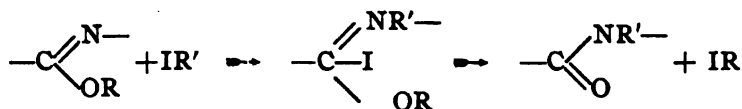
The more negative the radicals attached to nitrogen the less readily the rearrangement took place. Methyl iodide produced a rearrangement more readily than other halides. In the case of the acetylthioncarbamic esters only the methyl derivatives were found to undergo a molecular rearrangement.

It was shown that the aromatic imido esters, in general, readily undergo an analogous metastatic change,² while Dr. H. F. Mer-

¹ *Am. Chem. J.*, 22, 140 (1899); *Ibid.*, 24, 60, 189, 424 (1900).

² *Ibid.*, 23, 125 (1899); *Ibid.*, 23, 135 (1900).

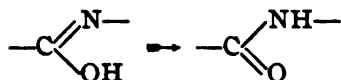
riam has found that the aliphatic members do not show a similar tendency. These molecular rearrangements were brought about catalytically with only a trace of alkyl halide, and here again methyl iodide acted the most readily. By employing a halide with a group different from R, it was shown that the change involved an addition of alkyl to nitrogen and then a separation from oxygen. This may be represented as follows:



The mechanism of the rearrangement of the thioncarbamic esters was previously shown by us to be similar.

Wislicenus and Goldschmidt¹ found that N-substituted imidoesters undergo a molecular rearrangement on simply heating alone to a high temperature, the imidoesters of Pinner being decomposed by this treatment.

We² have found that when R in the above formula is an acyl group, the rearrangement takes place by heat alone far more readily than when it is an alkyl group. In fact, some of these acyl derivatives (acyclo) undergo isomerization as readily as the parent substances, the pseudoforms of the amides.



It appears also that oxygenimidoanhydrides, $\begin{array}{c} \text{NR} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{OCOR}' \end{array}$, undergo a molecular rearrangement more readily than thioimidoanhydrides, $\begin{array}{c} \text{NR} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{SCOR}' \end{array}$, and that among these labile forms the cyclo derivatives, in general, show the greatest stability. Before we undertook the investigation of this subject, it was known that certain cycloimidoesters undergo a molecular rearrangement on heating.

The first observation of this sort was made by Hofmann and Olshausen,³ who showed that *o*-cyanuric methyl ester gave the

¹ *Ber. d. chem. Ges.*, 33, 1467 (1900).

² *Am. Chem. J.*, 30, July (1903).

³ *Ber. d. chem. Ges.*, 3, 272 (1870).

N-derivative on heating. Ponomaren¹ and Hofmann² then further investigated the subject. Haitinger and Lieben³ found that methoxypyridine gave methylpyridon, and Knorr⁴ found that methoxylepidine gave methyllepidon, facts which led Michael⁵ to state that all compounds having the grouping ROCN would give the isomeres OCNR on heating.

In the pyrimidine series, such rearrangements were afterwards observed by E. v. Meyer⁶ and by Pinner.⁷ Andreocci⁸ apparently found a similar case among the pyro- $\beta\beta'$ -diazoles. Knorr and Fertig⁹ further investigated the molecular rearrangement of alkyl-oxyquinoline derivatives by means of alkyl halides and showed that the reaction involved an addition. Wislicenus and Körber¹⁰ showed that the 8-alkyloxycaffeins also undergo a metastatic change on heating. This appears to be a complete list of these molecular rearrangements in the cyclo series.

In the acyclo series Gabriel and Neumann¹¹ found that by the action of heat benzimidochlorethyl ester is transformed into β -chlorethylbenzamide, and the mechanism of this reaction was shown to involve an inner addition with the formation of an intermediate five-membered ring, by Wislicenus and Körber.¹² Recently the work on the molecular rearrangements of acycloimidoesters has been greatly extended by Lander.¹³

It is probable that the mechanism of these rearrangements by heat alone is similar to that in the case of the action of alkyl halides. A small quantity of foreign material may act catalytically, by addition and then a separation.¹⁴ Or, under the influence of heat, this effect may take place within the molecule itself, as in the case of the molecular rearrangement of N-dialkylaminoesters into betaines.¹⁵

¹ *Ber. d. chem. Ges.*, 18, 3271 (1885).

² *Ibid.*, 19, 2061 (1896).

³ *Monatsh. Chem.*, 6, 323 (1885).

⁴ *Am. Chem. J.*, 236, 104 (1886).

⁵ *J. prakt. Chem.*, 37, 510 (1888).

⁶ *Ibid.*, 39, 271 (1889).

⁷ *Die Imidomether u. Ihre Derivate*, p. 215 (1892).

⁸ *Ber. d. chem. Ges.*, 24, R. 805 (1891).

⁹ *Ibid.*, 30, 922, 929; *Ibid.*, 30, 937 (1897).

¹⁰ *Ibid.*, 35, 1991 (1902).

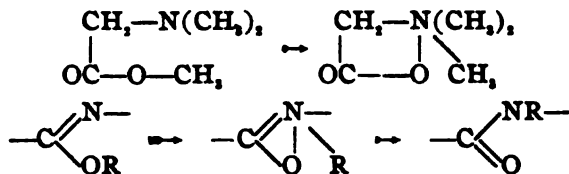
¹¹ *Ibid.*, 25, 2383 (1892).

¹² *Ibid.*, 35, 164 (1902).

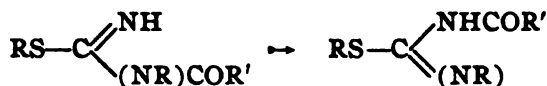
¹³ *J. Chem. Soc. (London)*, 83, 406 (1903).

¹⁴ Compare Lander: *Loc. cit.*, p. 414.

¹⁵ Willstätter: *Ber. d. chem. Ges.*, 35, 585 (1902).



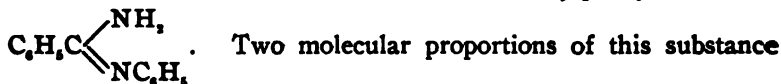
The three-membered, intermediate ring in the case of the imidoesters not being stable, the bonds shift and the stable amides are formed. In fact, this ring-formation is considered in a recent article,¹ by Kauffmann, to represent the structure of the pyridines. The molecular rearrangement of alkyloxypyridine derivatives therefore halts at what corresponds to the intermediate stage in other cases. Closely similar to these rearrangements are those of the imido acid anhydrides. Outwardly the molecular rearrangements of unsymmetrical acylthioureas, acylpseudothioureas² and their corresponding cyclo derivatives, the arylpseudothiohydantoins, appear to be similar:



In these cases the mechanism, however, probably involves the formation of an unstable, four-membered ring as an intermediate condensation product.³

All of the unsymmetrical acylthiourea and acylpseudothiourea derivatives, which have been investigated, undergo the above represented isomerization on melting, and some so readily that they cannot be crystallized by warming with alcohol. Similar results would be expected in the true amidine series.

We first selected for examination benzenylphenyl amidine,



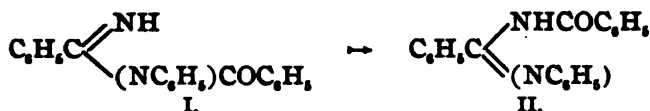
were slowly treated in cold ether with benzoyl chloride. On filtering from the precipitate of amidine hydrochloride which formed, and evaporating the ether spontaneously in a vacuum, a crystalline benzoyl derivative was obtained. This material, when carefully prepared, was homogeneous, and it had the structure represented by formula I. When allowed to stand for some time, or,

¹ *Ber. d. chem. Ges.*, 36, 1062 (1903).

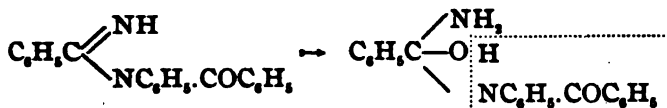
² *Am. Chem. J.*, 27, 270 (1902).

³ *Ibid.*, 28, 134 (1902).

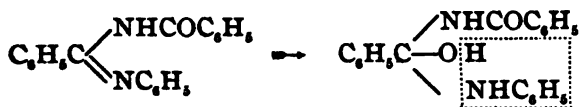
if an attempt was made to crystallize the substance from a hot solution, or if heated, it immediately underwent a molecular rearrangement into the isomeric benzoyl derivative, which is represented by formula II.



The proof of this rearrangement was obtained as follows: When the material obtained directly from the ether solution was treated with dilute hydrochloric acid it underwent hydrolysis and gave practically the calculated quantity of benzanilide and benzamide. No dibenzamide was obtained.



When another portion of the same preparation was warmed in a little alcohol for a few minutes on the steam-bath, and then treated with hydrochloric acid, the result obtained was precisely the reverse from the above; almost the calculated quantity of dibenzamide was obtained, while only a trace of benzanilide resulted. The hydrolysis took place in this case as follows:



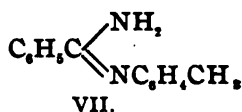
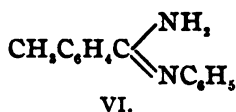
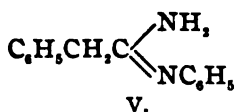
The molecular rearrangement of unsymmetrical benzoylbenzenylphenylamidines therefore took place with great ease and smoothness.

In our next experiment we employed the same benzenylphenylamidines, but used acetyl chloride instead of benzoyl chloride. In this case the product consisted of a mixture of the two following acetyl derivatives, corresponding to the above labile and stable benzoyl compounds.



The structure of these products was determined by hydrolysis as before with hydrochloric acid. The remarkable fact was then discovered that the unsymmetrical acyl derivative III was a perfectly stable substance. It showed no tendency to rearrange even at a temperature of 150°-160°. This flagrant breach of analogy, as Lachman¹ states in other cases, certainly calls for protest from the systematists.

We next examined the behavior of the three following isomeric amidines with benzoyl chloride: Phenylacetphenylamidine (V), *p*-tolenylphenylamidine (VI), and benzenylorthotolylamidine (VII).



Phenylacetphenylamidine (V) gave a mixture. This contained an unsymmetrical benzoyl derivative, which showed no tendency to undergo a molecular rearrangement. It could be repeatedly crystallized from alcohol and it could be heated above its melting-point without alteration.

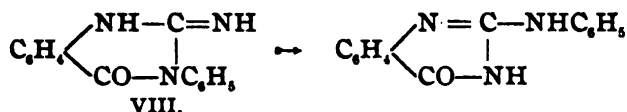
Paratolenylphenylamidine gave a mixture of the two isomeric benzoyl derivatives. That the unsymmetrical acyl derivative, contained in this mixture, readily undergoes a molecular rearrangement was shown by treating the product with dilute hydrochloric acid. Before heating, benzanilide was obtained; when the product was simply warmed on the steam-bath and then treated in the same manner with hydrochloric acid, no benzanilide resulted.

Benzenylorthotolylamidine gave the stable symmetrical amidine directly; the formation of an unsymmetrical derivative was not observed. These results show that the point of attack of acyl chlorides on the amidines differs in different cases and that both acyl derivatives may be formed together without involving a metastatic change. No conclusions as to whether a new unsymmetrical acyl amidine will or will not undergo a molecular rearrangement can be drawn from these experiments and no generalization can be made with the data at hand. The structure of the acyl amidines obtained gives no clue to the tautomeric form of the amidines beyond the probability that, in the cases where molecular rearrangements do take place,

¹ This Journal, 23, 907 (1901).

the structure of the amidine corresponds to that of the stable form of the acyl derivative. The results also emphasize how unsafe it is to predict from analogy. They suggest that perhaps similar results may be observed in other series, the closely analogous imido acid anhydrides, for example.

In the course of the work, we found that, if pyridine was present, on treating an amidine with an acylchloride that diacyl derivatives resulted. We also examined the behavior of a cycloacylphenylguanidine on heating, *viz.*, 2-amino-3-phenyl-4-ketodihydroquinazoline (VIII). From its similarity in structure to benzoylbenzylamidine and to the labile phenylpseudothiohydantoin, which readily undergoes a metastatic change at 100°, a molecular rearrangement might be expected to take place in this case as follows:



The material, however, proved to be quite stable and it sublimed unaltered at a high temperature.

EXPERIMENTAL PART.

Unsymmetrical Benzoylbenzylphenylamidine was prepared by slowly treating two molecular proportions of benzenylphenylamidine in ice-cold, dry ether with benzoyl chloride. The ether solution was then filtered and the filtrate evaporated in a vacuum. The crystalline mass thus produced, after washing with a little cold alcohol, melted at about 95°-97°, when carefully prepared. In a number of preparations it melted somewhat higher but then it was found to contain more or less of the isomeric symmetrical derivative. A nitrogen determination gave 9.8 per cent. nitrogen. Calculated for $\text{C}_{12}\text{H}_{10}\text{ON}_2$, 9.3 per cent. When an attempt was made to purify the material by crystallizing from alcohol, it underwent a molecular rearrangement into symmetrical benzoylbenzylphenylamidine (melting-point 143°), which has already been described in a paper from this laboratory.¹

Action of Hydrochloric Acid.—The material melting at 95°-97° (0.95 gram) was treated with 2 cc. of alcohol and 2 cc. of 22 per cent. hydrochloric acid. The amidine dissolved and then a mass of crystals separated; the whole was warmed to boiling, cooled

¹ *Am. Chem. J.*, 20, 573 (1898).

and then treated with 9 cc. of 15 per cent. sodium hydroxide solution. The insoluble material was washed with 12 cc. of water; it melted at 156°-159° and it weighed 0.60 gram. This proved to be benzanilide, the calculated quantity of benzanilide being 0.62 gram. On acidifying the alkaline solution with acetic acid no precipitate was formed. This shows the absence of dibenzamide and of the symmetrical benzoyl derivative in the original material. On shaking the solution with ether, benzamide was extracted.

Behavior on Heating.—Another portion of the benzoyl derivative melting at 95°-97° (0.95 gram) was warmed on the water-bath in 10 cc. of alcohol for a half hour. The alcohol was then evaporated and the varnish obtained was treated with 2 cc. of hydrochloric acid as above, except that no alcohol was used. On gently warming, the varnish solidified to a mass of colorless needles. When washed with water and dried, this weighed 0.62 gram. This all dissolved in 5 cc. of 15 per cent. alkali diluted with 5 cc. of water, except 0.03 gram of material, and was precipitated by acetic acid. It melted at 145°-147° and had all the properties of dibenzamide, the yield being about 87 per cent. of the calculated. These results prove conclusively that a rearrangement of the unsymmetrical benzoyl derivative took place on heating.

Unsymmetrical Acetylbenzylphenylamidine.—The product, in this case, on evaporating the ether, formed a varnish which finally solidified. It then melted at about 114° and when mixed with acetanilide the melting-point was lowered to 90°-95°. It crystallized from alcohol in the form of colorless prisms and then melted at 128°-129°; when this was mixed with benzamide the melting-point was lowered to 110°. A nitrogen determination gave 11.41 per cent. nitrogen. Calculated for $C_{15}H_{14}ON_2$, 11.76 per cent. The alcoholic mother-liquors from the above were allowed to stand at ordinary temperature, whereupon prisms of the symmetrical acetylbenzylphenylamidine melting at 138°-139° were obtained. This was described in a previous article.¹

Action of Hydrochloric Acid.—The above acetyl derivative melting at 128°-129° was warmed in alcohol with hydrochloric acid, the alcohol was evaporated, and the residue on crystallizing from water gave plates of acetanilide melting at 112°-113°.

¹ *Am. Chem. J.*, 20, 574 (1898).

Behavior on Heating.—The acetyl derivative, which was proved to have an unsymmetrical structure by the above experiment, was heated at various temperatures and finally for two hours at 150°-160°. A slight decomposition took place, but on crystallizing from benzene unaltered material was obtained. When mixed with the symmetrical derivative the melting-point was lowered to 108°-115°. There was no evidence of a rearrangement having taken place. Owing to the difficulty with which the following amidines dissolve in ether, chloroform was tried as a solvent in some of the experiments. The results were not satisfactory, as decomposition products were formed which interfered with the isolation of the acyl amidines. The best results were obtained when the amidines were simply suspended in dry ether and allowed to stand for some time with the required amount of benzoyl chloride.

Benzoylphenylacetamide, $C_6H_5CONHCOCH_2C_6H_5$.—This was formed along with benzanilide and other products when phenylacetphenylamidine was treated with benzoyl chloride in chloroform. The hydrochloric acid salt of the amidine did not separate in this case but was removed in the subsequent treatment with water. The product was a semi-solid mass which, when dissolved in benzene, gave benzanilide and then colorless prisms which, after several recrystallizations, melted at 129°-130°. A nitrogen determination agreed with the calculated for benzoylphenylacetamide. Calculated for $C_{18}H_{15}O_2N$, 5.8 per cent. Found, 6.1 per cent. The material was soluble in cold alkali.

Unsymmetrical Benzoylphenylacetphenylamidine.—Ten grams of phenylacetphenylamidine were suspended in 100 cc. of dry ether, and after 3.3 grams of benzoyl chloride had been added the mixture was allowed to stand four hours. The solid material then removed by filtration was found to dissolve completely in water and was therefore the hydrochloric acid salt of the amidine. After the ether solution was evaporated, a gum remained which did not crystallize on standing. When dissolved in alcohol, it gave colorless plates which, after three recrystallizations from alcohol, melted at 110°-111°. The liquid was slightly cloudy up to 118°. A nitrogen determination gave results agreeing with the calculated for a monobenzoylphenylacetphenylamidine. Calculated for $C_{21}H_{18}ON_2$, 8.9 per cent. Found, 8.6 per cent.

Action of Hydrochloric Acid.—One-half a gram of the material melting at 110° - 111° was treated with hydrochloric acid, as in the previous cases, whereupon the leaf-like crystals of benzanilide were obtained, melting at 157° - 158° . When this benzoyl derivative was heated above its melting-point (140°) and then crystallized from alcohol, the melting-point rose to 122° - 123° , but, on treating this material with hydrochloric acid, little or no benzoylphenylacetamide was obtained.

Dibenzoylphenylacetphenylamidine was prepared by mixing in chloroform, 4.4 grams of the amidine, 1.6 grams of pyridine and 2.9 grams of benzoyl chloride, the latter diluted with ether. The precipitate which formed consisted of the hydrochloride of the amidine. The chloroform contained material which, on crystallizing from alcohol, formed colorless prisms and melted at 175° . A nitrogen determination gave 7.2 per cent. nitrogen. Calculated 6.7 per cent. When treated with hydrochloric acid, benzanilide, phenylacetamide and benzoic acid were obtained.

Symmetrical Benzoylparatolcnylphenylamidine.—Paratolcnylphenylamidine (6.1 grams) suspended in 100 cc. of dry ether was treated with 2 grams of benzoyl chloride in 25 cc. of ether. The mixture was allowed to stand for three hours. On filtering and evaporating the ether, a gummy mass was obtained which, on crystallizing from alcohol, gave clusters of colorless prisms melting at 126° . A nitrogen determination showed that this substance was a monobenzoylparatolcnylphenylamidine. Calculated for $C_{21}H_{18}ON_2$, 8.91 per cent. Found, 8.82 per cent.

Action of Hydrochloric Acid.—One gram of the material was suspended in alcohol and warmed with a few drops of hydrochloric acid. On standing, colorless needles separated which, on crystallizing from alcohol melted sharply at 112° - 113° . A nitrogen determination indicated that this substance was *paratolcnylbenzamide*, $CH_3C_6H_4CONHCOC_6H_5$. Calculated for $C_{15}H_{13}O_2N$, 5.85 per cent. Found, 6.34 per cent. That this was the diacyl amide was further shown by the fact that the material dissolved in alkali and was decomposed into paratoluic amide melting at 151° - 157° . The unsymmetrical benzoyl derivative in this case was not isolated in a state of purity. That it was present in the gummy mass described above was shown by the fact that benzanilide was obtained when the product was treated with dilute hydrochloric

acid. A portion of the crude reaction product was warmed on the steam-bath and then treated with hydrochloric acid, whereupon no benzanilide was obtained.

Dibenzoylbenzenylorthotolylamidine.—Ten grams of benzenyl-orthotolylamidine were suspended in 100 cc. of dry ether and treated with 3.3 grams of benzoyl chloride in 20 cc. of ether. The mixture was then allowed to stand over night. The amidine hydrochloride which separated was mixed with some material which did not dissolve when the mixture was treated with water. When this material was crystallized from alcohol, colorless, beautiful, diamond-shaped plates were obtained, melting sharply at 167° . A nitrogen determination showed that this material was a dibenzoyl derivative: Calculated for $C_{28}H_{22}O_2N_2$, 6.7 per cent. Found, 7.0 per cent. When this substance was treated with dilute hydrochloric acid in alcohol, crystals of benzorthotoluide separated melting at 142° .

Symmetrical Benzoylbenzenylorthotolylamidine.—On evaporating the ether solution from the above dibenzoyl derivative, a varnish was obtained. From this, on crystallizing from alcohol, colorless prisms were obtained melting at 111° – 113° . A nitrogen determination gave 8.9 per cent. Calculated for $C_{21}H_{15}ON_2$, 8.9 per cent.

Action of Hydrochloric Acid.—A gram of the substance was treated with dilute hydrochloric acid (2 cc.) and 2 cc. of alcohol. From this solution long, colorless needles of dibenzamide separated, melting at 148° . When these needles were mixed with dibenzamide the melting-point was not lowered.

Orthophenylguanidinebenzoic Acid,

$\text{NH}_2\text{C}(\text{NH})-\text{NHC}_6\text{H}_5$. —In the course of some experi-

ments with pseudothiureas we heated orthoaminobenzoic acid with phenylpseudomethylthiurea and obtained a product which crystallized from alcohol in colorless prisms, melting at 248° . This material was not dissolved at first by sodium hydroxide or hydrochloric acid, but on standing in these solvents it underwent a change, being converted into a substance, crystallizing in hair-like needles from alcohol, melting at 256° . This latter material was readily soluble in alkali, and a nitrogen determination gave

results agreeing with the calculated for 2-anilino-4-ketodihydro-

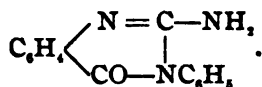
quinazoline, $C_6H_5 \begin{matrix} \diagup N = C.NHC_6H_5 \\ \diagdown CO-NH \end{matrix}$. Found, 17.67 per cent.

Calculated for $C_{14}H_{11}ON_3$, 17.72 per cent.

At this point we were unable to decide whether the above product first obtained, melting at 248° , underwent a direct condensation into the above quinazoline derivative soluble in alkali, or whether it first condensed to give the isomeric 2-amino-3-phenyl-4-ketodihydroquinazoline, which would be insoluble in alkali, this then undergoing a molecular rearrangement into the above quinazoline, melting at 256° . To decide this question we prepared 2-amino-3-phenyl-4-ketodihydroquinazoline from 2-Chlor-3-phenyl-4-ketodihydroquinazoline.—This chloride was prepared from 2-thio-3-phenyl-4-ketotetrahydroquinazoline by following the directions of McCoy.¹

McCoy obtained this chloride, but did not purify the substance. We found that the oil first obtained solidified and could be crystallized from alcohol. It then formed colorless prisms and melted at 132° . It was analyzed with the following results: Calculated for $C_{14}H_9ON_2Cl$, 10.9 per cent. nitrogen. Found, 10.7 and 11.1 per cent.

2-Amino-3-phenyl-4-ketodihydroquinazoline,



The above chloride was heated in a closed tube at 120° - 130° with an excess of alcoholic ammonia. The product crystallized from alcohol in colorless prisms and melted at 237° - 238° . It was insoluble in sodium hydroxide, as was expected, and a nitrogen determination gave: 17.50 per cent. nitrogen. Calculated for $C_{14}H_{11}ON_3$, 17.72 per cent. When this material was boiled with dilute hydrochloric acid, complete solution finally took place and, on cooling, 3-phenyl-2,4-diketotetrahydroquinazoline² separated. When the above cyclocacylguanidine was heated above its melting-point (in a bath at 250°), it simply sublimed unaltered without undergoing any molecular rearrangement.

¹ Ber. d. chem. Ges., 30, 1691 (1897).

² Busch: J. prakt. Chem., 51, 265 (1895); Paul: Ber. d. chem. Ges., 27, 978 (1894).

NEW HAVEN, CONN., May 26, 1903.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY
OF NORTH CAROLINA.]

MERCUROUS SULPHIDE.

BY CHAS. BASKERVILLE.

Received May 25, 1903.

IN the paper "On the Reactions between Mercury and Concentrated Sulphuric Acid,"¹ by F. W. Miller and the writer, two statements were made, which, while true for the conditions given, require modification in the light of knowledge recently gained. "The reaction is by no means like that of copper"² (p. 874) and "No sulphide was produced, nor any free sulphur" (p. 876). By great variations of one of the factors, time, sulphide was obtained. The experiment was continued through a period of five years and one week. Ten grams of pure mercury³ were covered with 50 grams of chemically pure sulphuric acid (99.65 per cent.) in a well-ground, glass-stoppered bottle of about 100 cc. capacity and allowed to remain at the temperature of the laboratory (never over 30° C.) for the period mentioned. While the bottle was never subjected to the direct rays of the sun, no attempt was made to shield it from the light.

When the bottle was opened, there was a strong outward pressure, and noticeable quantities of sulphur dioxide escaped. This corroborates the statements put forward in our second paper⁴ in controversion of the criticism of Pitman.⁵ Morley⁶ and Berthelot⁷ have also shown, independently, that mercury and sulphuric acid of maximum concentration react at ordinary temperatures with the evolution of sulphur dioxide.

The point of especial interest in the experiment lay in the simultaneous formation of a sulphide of mercury, which showed that the mercury resembles copper in this reaction more than was thought. Upon the bright metal there separated flakes, which resembled plates, of mercurous sulphide. The acid was decanted, a large volume of water added and quickly decanted. This was

¹ This Journal, 19, Nov., 1897.

² *Ibid.*, 17, Nov., 1895, and 18, Nov., 1896.

³ *Loc. cit.*

⁴ This Journal, 20, 515.

⁵ *Ibid.*, 20, 100.

⁶ *Loc. cit.*

⁷ *Chem. News*, 76, 325; *Compt. rend.*, 128, 20.

done several times. The bottle was inclined and revolved so that most of the sulphide was caused to cling to the sides of the vessel, the metallic mercury poured out and the sulphide thrown upon a filter and washed with alcohol (95 per cent.) until the wash-water was no longer acid. The brownish black plates (about 0.2 gram) were dried at 110° C. and analyzed by Mr. R. O. E. Davis of this laboratory.

Amount taken.	Sulphur found. Per cent.	Mercury found. Per cent.	Calculated for Hg ₂ S.
0.0866	8.23	7.41
0.0707	...	91.94	92.59
Total	...	100.17	100.00

The quantity remaining was too small to examine for the presence of free sulphur, although from the analysis it appears that 0.82 per cent. of free sulphur was present. As no quantitative determination of the sulphur dioxide, mercury sulphates produced, and so forth, were made, it is impossible to indicate the course of the reaction by an equation.

Authoritative works (Richter, Dammer, etc.) state that mercurous sulphide is not definitely known. Berzelius¹ said the black precipitate produced by hydrogen sulphide with mercurous salts was mercurous sulphide, but Barfoed² has shown that it is a mixture of mercuric sulphide and mercury. Antony and Sestini³ state that hydrogen monosulphide acting upon mercurous salts below 0° C. give mercurous sulphide, which above that temperature decomposes into mercuric sulphide and mercury.

Mercurous sulphide heated in a closed tube turns white (doubtless due to oxidation), becomes slightly yellow, then melts to a dark orange-brown liquid, which changes to a white solid on cooling, as does mercurous sulphate.

¹ *Archiv. d. Apothekervereins im nördl. Deutschland, von Brandes*, 18, 292.

² *J. prakt. Chem.*, 93, 230.

³ *Gazz. chim. Ital.*, 24, I, 193.

THE ACTION OF METALLIC MAGNESIUM UPON AQUEOUS SOLUTIONS.

BY CHARLOTTE F. ROBERTS AND LOUISE BROWN.

Received May 27, 1903.

The paper read by Mr. Kahlenberg on the above subject, at the Washington meeting of the American Chemical Society, interested us so much that we undertook a few simple experiments in the same line for ourselves. Since his paper has appeared in print¹ we find that in a few particulars our results differ from his and that our experiments have been carried on along somewhat different lines, and it has therefore seemed possible that our results also might be of interest to others.

In all of our experiments the *modus operandi* was the same. A 100 cc. gas-measuring tube was filled with the solution to be employed. In the mouth of this tube a one-holed rubber stopper was inserted, and a piece of magnesium ribbon was held in place in the solution by fastening it to the stopper with a bit of cheesecloth and some thread. The whole was then set up, in most cases in a tall jacket containing more of the same solution, for convenience in measuring, frequently, the volume of the gas under atmospheric pressure. The magnesium used was the magnesium ribbon manufactured by Schuchardt, and in our experiments the solution was always in excess. We used in most of our experiments an amount of magnesium equivalent to about 50 cc. of gas, or a piece about 8 cm. in length.

The most important particular in which our results differed from those of Mr. Kahlenberg was in the action of magnesium on distilled water. We found that if we used ammonia-free water, freshly boiled to drive out dissolved gases, no gas collected in the tube. The experiment was tried first with a short strip of magnesium ribbon and left standing for a week. It was then repeated with a strip of magnesium ribbon 50 cm. in length and left standing for four weeks. The magnesium appeared slightly tarnished, but no trace of gas was visible at the end of that time. When *unboiled* distilled water was used, in the same length of time, with much smaller amounts of magnesium, varying amounts

¹ This Journal, 28, 380.

of gas, from 2 to 3 cc., were collected. These results are apparently in opposition to those obtained by Bryant, who states that boiled and unboiled water have the same effect on magnesium.¹

The experiment was tried of taking some of the pure boiled distilled water and passing a current of oxygen through it before setting up the apparatus. In this case gas began to collect after standing twenty-four hours, and in the course of two weeks, 2.7 cc. of gas had collected from a strip of magnesium about 8 cm. in length. When a similar experiment was tried, using carbon dioxide instead of oxygen, the escape of gas was, as might have been expected, very rapid, the rate being greatest at first and decreasing with the time, as with other acids.

The principal facts indicated by our experiments seem to be:

(1) That magnesium is without action on distilled water, boiled to free it from gases and carefully cooled out of contact with air.

(2) That magnesium acts on undistilled water and on unboiled distilled water, setting free varying amounts of gas; also on water boiled and afterward charged with oxygen or carbon dioxide.

(3) That the hydrogen equivalent of magnesium can be obtained from aqueous solutions of varying strengths of the chlorides of sodium, potassium, magnesium, barium, calcium and strontium; also very slowly from the sulphate of magnesium (probably also of sodium and potassium); also from such dilute solutions of hydrochloric and sulphuric acids as contain in themselves but a small proportion of the hydrogen liberated.

(4) That with the same surface of magnesium the action of the chlorides is much more rapid than that of the corresponding sulphates. With chlorides of the same metal, the rate is dependent upon the concentration, though no strict proportionality can be traced. The maximum rate is more quickly attained in the stronger solution than in the weaker and is greater in amount, but the length of time for completing the reaction does not differ very much in the two cases.

(5) With equimolecular solutions of chlorides of sodium, potassium, magnesium, calcium, strontium and barium, the order of rapidity of action upon magnesium ribbon in our experiments was as follows: Magnesium, barium, strontium, calcium, sodium and potassium.

¹ *Chem. News*, Nov. 3, 1899.

In such experiments as these it is, of course, impossible to determine exactly the end-point of the reaction or to measure with any accuracy the rate of the reaction as it approaches completion. Occasional tapping of the tube is necessary to liberate the last portions of gas, and there is always the possibility that some magnesium may be covered by the precipitate and left unacted upon. We observed, however, what was mentioned by Mr. Kahlenberg, *viz.*, that the coating of precipitate over the magnesium did not retard the action as much as might have been expected. Even when the magnesium ribbon appeared to be entirely crusted over, the reaction went on until approximately the hydrogen equivalent of the magnesium had been collected. It is true that the results as shown in the following tables run a little low, but considering the possible sources of error, they seem near enough to justify the statement that the hydrogen equivalent may be set free in all cases.

TABLE I.
(Solutions contained $\frac{1}{10}$ gram-mol. per liter.)

	Weight of magnesium calculated from gas.	Weight of magnesium taken.
MgCl ₂	0.0538	0.0539
KCl	0.0535	0.0539
NaCl	0.0525	0.0539
BaCl ₂	0.05345	0.0540
CaCl ₂	0.05276	0.0534
SrCl ₂	0.0526	0.0534
MgSO ₄	0.0530	0.0539

Although but one result is given, confirmatory experiments were made in almost every case.

The time required for the completion of the reaction, with the amounts above given, was from twenty-four to forty-eight hours in the case of the chlorides, but in the case of the sulphates was much greater. The sulphates of sodium, potassium and magnesium were all tried, and the one which acted most rapidly was magnesium. With this it took nearly four weeks to get the result above given. With the sulphates of sodium and potassium the action was so slow that the experiment was discontinued before the reaction was completed.

That very dilute solutions of the chloride of magnesium are adequate to set free the hydrogen equivalent of the magnesium is indicated by our experiments with very dilute hydrochloric

acid. The acid used was of such strength that from 100 cc. only 8.1 cc. of hydrogen could be set free. The tube was inverted in a small dish containing more of the same liquid, and this might increase the possible yield of hydrogen by a small amount. The apparatus was left standing for a week, although the operation was probably completed a little before that time. At the end of a week, the volume of hydrogen was 52.5 cc. at a temperature of 19°C . and pressure of 765 mm. This corresponds to 0.0540 gram of magnesium, and the weight of magnesium taken was 0.0539 gram. A study of the rate of this reaction per twenty-four hours is interesting.

TABLE II.

	Volume of gas collected.	Volume increment per hour.
1st 24 hours	5.2	0.22
2nd 24 hours.....	7.8	0.1
3rd 24 hours	17.6	0.4
4th 24 hours	29.8	0.5
8 hours later.....	35.1	0.66
6th 24 hours	48.0	0.32
7th 24 hours	52.5	0.19

The relation between the time and the amount of gas collected is therefore represented by the following curve:

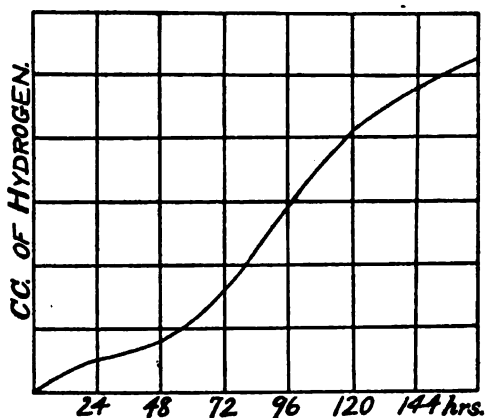


Fig. 1.

It will be noticed that the *rate* of the reaction at first decreases with the time, as is usual with the action of an acid on a metal; then, when an amount of gas has been collected nearly equal

to the amount calculated as contained in the hydrochloric acid used, the rate increases until it reaches a maximum and then decreases in about the same way as has been observed when the metal was put directly into a solution of magnesium chloride. In this case, when the rate began to increase, the amount of magnesium which had gone into solution as magnesium chloride can not have been greater than 10 milligrams.

As has just been indicated, we observed that the curve showing the relation between the time and the volume increment in a given time was distinctly different in the case of the action of acid in excess upon magnesium, and the action of aqueous solutions of chlorides. This is shown in the following table:

TABLE III.

	HCl. (Weight magnesium taken = 0.0536.)		MgCl ₂ 1/6 molecule per liter (Weight magnesium taken = 0.0539.)	
	Volume of gas.	Rate per hour.	Volume of gas.	Rate per hour.
1 hour	11.6	11.6	0.9	0.9
2 hours	18.2	6.6	3.9	3.0
3 "	21.8	3.6	8.7	4.8
4 "	24.1	2.3	13.3	4.6
5 "	26.1	2.0	17.6	4.3
6 "	27.7	1.6	21.3	3.7
7 "	24.8	3.5
8 "	28.3	3.5
9 "	31.6	3.3
10 "	34.2	2.6
11 "	36.4	2.2

These data and corresponding ones in regard to certain other solutions are represented in the following curves, which show how the volume increment per hour changes as time advances. It will be observed that the acid-rate curve is a rapidly descending one, according to the law of mass action, whereas in the case of the chlorides, the curve ascends in each case until it reaches a maximum and then descends slowly.

The maximum rate depends upon the particular chloride employed and upon the strength of the solution. With different concentrations of the same salt, the maximum rate is higher in the case of a strong solution than with a weak one and is, in general, more quickly attained. The curves also show that after the maximum rate has been reached, there is a tendency for the rates to approach one another, so that after four or five hours, the volume

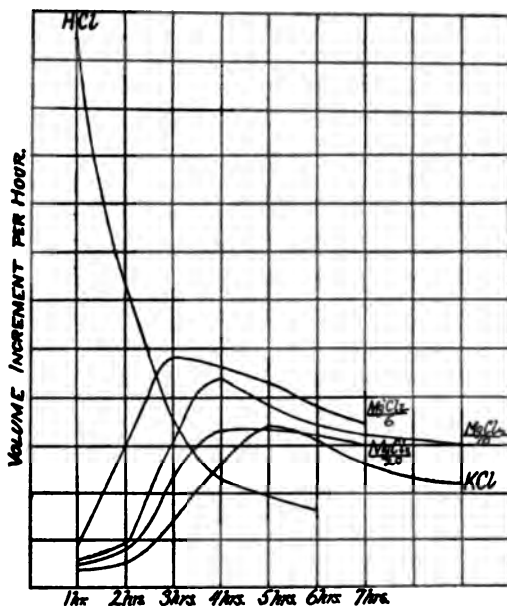


Fig. 2.

increments per hour do not vary much with the different concentrations.

Although Mouraour and others have stated that the action of magnesium on solutions of the alkaline earth metals is feeble, it was not our experience that the rate of the reaction with these substances fell so very far behind that on solutions of the same strength of magnesium chloride. In order to compare the rates of action of the chlorides of the alkali and alkaline earth metals, solutions containing $\frac{1}{10}$ gram-mol. per liter were set up as nearly as possible at the same time; pieces of magnesium ribbon 33 cm. long were used and observations taken every half hour. A solution of magnesium chloride containing $\frac{3}{10}$ gram-mol. per liter was also used. The results of these experiments are expressed in the following table:

TABLE IV.
Volume of gas collected.

	KCl.	NaCl.	CaCl ₂ .	SrCl ₂ .	BaCl ₂ .	MgCl ₂ .	$\frac{3}{10}$ MgCl ₂ .
1 hour.....	0.7	1.7	2.2	2.3	3.0	3.3	3.2
2 hours.....	3.5	5.6	6.6	7.0	9.9	11.6	13.8
3 ".....	9.0	11.8	13.2	14.3	21.2	24.6	29.8
4 ".....	16.6	19.5	22.7	24.1	34.4	37.5	42.4

	KCl.	NaCl.	CaCl ₂ .	SrCl ₂ .	BaCl ₂ .	MgCl ₂ .	² / ₁₀ MgCl ₂ .
5 hours.....	25.0	27.4	32.1	33.8	45.5	48.7	54.0
6 "	33.8	35.3	41.0	43.0	55.3	59.3	64.8
7 "	41.6	42.6	48.8	51.6	64.3	69.6	74.6
8 "	49.4	56.0	59.8	72.5	78.4	83.4

Volume increment per hour.

	KCl.	NaCl.	CaCl ₂ .	SrCl ₂ .	BaCl ₂ .	MgCl ₂ .	² / ₁₀ MgCl ₂ .
1 hour.....	0.7	1.7	2.2	2.3	3.0	3.3	3.2
2 hours.....	2.8	3.9	4.4	4.7	6.9	8.3	10.6
3 "	5.5	6.2	6.6	7.3	11.3	13.0	16.0
4 "	7.6	7.7	9.5	9.8	13.2	12.9	12.6
5 "	8.4	7.9	9.4	9.7	11.1	11.2	11.6
6 "	8.8	7.8	8.9	9.2	9.8	10.6	10.8
7 "	7.8	7.3	7.8	8.6	9.0	10.3	9.8
8 "	6.8	7.2	8.2	8.2	8.8	8.8

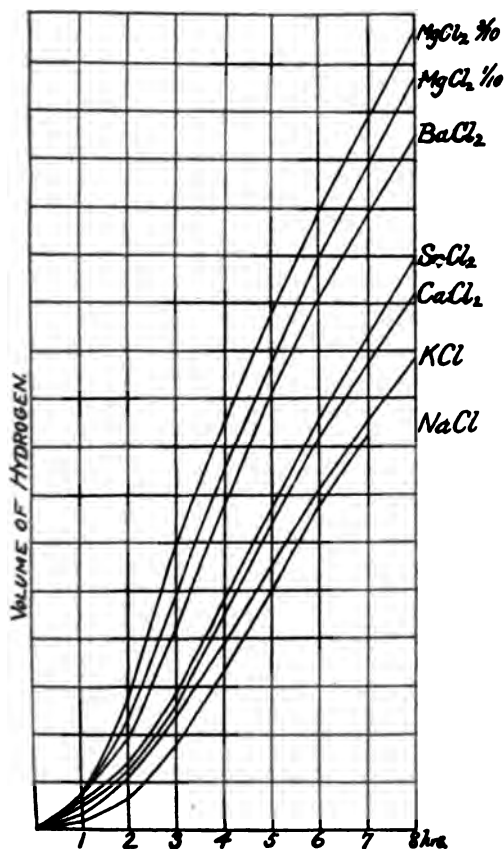


Fig. 3.

The curves representing the relation between the time and the volume of gas collected show at a glance the similarity in action of the sodium and potassium chlorides, and also of the chlorides

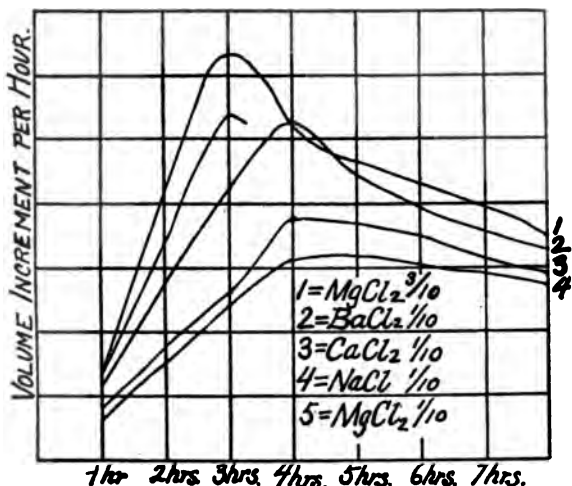


Fig. 4.

of calcium and strontium, but that the action of the barium salt is more nearly like that of the magnesium chloride than like that of the other alkaline earth chlorides. It will be noticed that the chloride of magnesium attains its maximum rate in the third hour, the salts of the alkaline earth metals in the fourth hour, and of sodium and potassium in the fifth and sixth hours; also that the sodium begins more rapidly than the potassium, but that the potassium gradually gains upon the sodium. In all cases, the *rate* of the reaction at first increases and then decreases, as is shown in the accompanying graphic representation of the relation between the time and the volume increments per hour. The potassium and strontium curves are omitted because they correspond so nearly with the sodium and calcium, and the curve of the weaker magnesium chloride solution is only given in part, because, after passing the maximum, it coincides in various parts with the barium chloride and the stronger magnesium chloride. It is noteworthy that the curves, which reach the highest maxima, descend the most rapidly, and therefore there is a tendency to approach a uniform rate. It should perhaps be mentioned that the hydrogen equivalent of the magnesium used would be about 200 cc., so that these observations were made only during the first part of the reaction.

The persistency of type of the rate curve in all these salts, consisting as it does of an ascending and then a descending portion, seems to us of sufficient importance to be taken into account in any explanation of the phenomenon.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY
OF CINCINNATI, No. 59.]

A METHOD FOR THE DETECTION OF CHLORIDES, BROMIDES AND IODIDES.¹

BY STANLEY BENEDICT AND J. F. SNELL.

Received June 5, 1903.

THE problem of the detection of chlorides, bromides and iodides in presence of each other is one to which a great deal of attention has been devoted, and the present proposal of a new method is justified only by the conviction of the authors that in simplicity of execution, in reliability and in delicacy this method is superior to any hitherto proposed.

Like many of the methods proposed in the past, the one here presented is based upon the varying ease of oxidation of the halogen acids. It arose from a reasonably successful attempt to use dilute nitric acid as the oxidizing agent. Concentrated nitric acid, added dropwise, was employed for this purpose by Kebler,² who states that during a five years' trial by students it gave very satisfactory results. We have found that if nitric acid of suitable dilution is used, it is indeed possible to boil a mixture of the halogen salts with it long enough to liberate and expel all the iodine and bromine without any noticeable loss of chlorine. We may cite here two out of about twenty-five experiments. The acid was of five times molar strength and the quantity used was about half the volume of the solution to be tested:

1. Cl detected in a mixture of 49.9 cc. N KBr and 0.1 cc. N NaCl.

2. Cl detected in a mixture of 10 cc. N/100 KI, 9.8 cc. N/100 KBr, and 0.3 cc. N/100 NaCl.

The substitution of dilute for concentrated nitric acid obviates one defect in Kebler's method, *viz.*, that the concentration of the

¹ Read before the Cincinnati Section of the American Chemical Society, May 13, 1903.

² *J. Anal. Appl. Chem.*, 6, 569 (1892).

acid in the test solution was not well enough controlled, but there are at least two objections that apply to the method, even when the dilute reagent is used, *viz.*, that the separation between iodide and bromide is by no means sharp and that in some instances iodic acid is formed in sufficient quantity to give a precipitate with silver nitrate resembling silver chloride. In the course of the experiments referred to above we observed in several instances that a solution of pure potassium iodide, after boiling with dilute nitric acid until colorless, would give with silver nitrate a white precipitate, soluble in ammonium hydroxide (therefore not iodide) and that this precipitate was not obtained from another portion of the decolorized solution after neutralizing with ammonia, acidifying with oxalic acid, evaporating to dryness and redissolving in nitric acid (therefore iodate). Another fact noticed in the course of these experiments was that a solution containing both potassium bromide and potassium iodide was decolorized somewhat more quickly than a solution of bromide alone. This also pointed to the conclusion that some iodic acid was formed by the action of the nitric acid on the liberated iodine, for the hydrobromic acid would be oxidized more readily by iodic than by nitric acid.

It was the above-mentioned observation that led to the use of the reagent proposed in our present method, *viz.*, iodic acid in the form of potassium iodate. This oxidizing agent will not react with any of the halide ions in neutral solution, but will liberate iodine from potassium iodide in acetic acid solution, while the bromine of potassium bromide is not at all liberated, except upon addition of a stronger acid. As the stronger acid for liberating the bromine we employ nitric acid (dilute) for the two reasons that in the presence of this acid it is easy to eliminate any excess of potassium iodate and that, on the other hand, should the quantity of potassium iodate added be insufficient to react with all the bromide, the nitric acid is itself capable of effecting a complete separation. The first reason is the main one, as, in general, the quantity of potassium iodate added will be sufficient to react with all the bromide.

According to Fresenius,¹ the use of iodic acid or of potassium iodate and hydrochloric acid as a reagent for iodides was proposed by Liebig. Fresenius objects that the reagent "must be

¹ "Qualitative Analysis," Wells' translation (1897), p. 380.

used with the greatest caution" because "an excess of iodic acid will at once put an end to the reaction." It is obvious that this objection applies only to the use of the iodate *with hydrochloric acid*, the liberated iodine combining with the chlorine to form iodine chloride. In the absence of hydrochloric acid no such difficulty exists. Another objection made by Fresenius is that reducing agents will liberate iodine from the reagent, thus causing confusion. In reply to this objection we would point out that the halogen acids can be easily separated from all the other common acids, with the exception of sulphocyanic, by precipitating in presence of nitric acid with silver nitrate and reducing the precipitate with zinc and sulphuric acid.¹ The silver sulphocyanate could easily be destroyed by igniting the precipitate before reducing it, but this is unnecessary. In the presence of sulphocyanate, the test for iodide may be made (after neutralizing) by adding first sodium acetate and then acetic acid and potassium iodate. It is a familiar fact that the acidity of acetic acid is diminished by the addition of sodium acetate, the increase in the concentration of the acetate ion causing a depression of the dissociation of the acid. In such a solution, *i.e.*, in one containing an extremely low concentration of hydrogen ions, the reaction between the sulphocyanate and iodate is entirely prevented, while that between the iodide and iodate still takes place.

Both of the reagents that Fresenius mentions, *viz.*, free iodic acid and potassium iodate with hydrochloric acid, have, of course, the further disadvantage that they cannot be used in presence of bromides, since they liberate bromine as well as iodine. But potassium iodate with acetic acid is free from this objection, as well as from those raised by Fresenius and has the obvious advantages over the commonly employed reagent, chlorine water, that the quantity of iodine liberated is one-fifth greater and that there is absolutely no danger of decolorization of the liberated iodine by excess of the reagent. For the detection of bromides, potassium iodate with nitric acid has similar advantages over chlorine water, the danger of decolorization by excess being absent and six halogen atoms being liberated instead of five, but here we have the additional advantage that the sixth halogen atom is iodine instead of bromine and that consequently the color imparted to the solution, whether in water, carbon disulphide or chloroform, is more intense.

¹ See Bailey and Cady's "Qualitative Analysis," (1901), p. 209.

The superior delicacy of the iodate reagent indicated by the above considerations is amply borne out by the results of actual tests. Thus, using 5 cc. of solution and shaking with about 1 cc. of freshly decolorized carbon disulphide, we were able to detect iodine by use of potassium iodate and acetic acid in an N/60,000 solution of potassium iodide without failure and in one trial out of two in an N/90,000 solution, while chlorine water gave a very faint test upon the third trial with an N/40,000 and failed entirely with an N/50,000 solution. Testing in the same manner for bromides, using potassium iodate and dilute nitric acid, we obtained coloration of the disulphide from an N/16,000 solution of potassium bromide on warming slightly, while chlorine water gave the test in an N/2,500 solution (which is about the delicacy claimed by Fresenius, *viz.*, 1 part of bromine to 30,000 of solution),¹ while it failed entirely with an N/4,000 solution. It would appear from these results that the iodate is nearly twice as delicate a reagent as chlorine water for iodides and four or five times as delicate a reagent for bromides, and with freshly decolorized carbon disulphide is capable of detecting iodine in 5 cc. of a solution containing 1 part of iodine in 500,000 of solution and bromine in 5 cc. of a solution containing 1 part of bromine in 200,000 of solution. It may be remarked in this connection that while the color test for iodine or bromine is decidedly more delicate with carbon disulphide than with chloroform, the latter reagent is sufficiently delicate for ordinary purposes and is, perhaps, preferable as a laboratory reagent because it does not become colored on standing.

METHOD.

The separation of the three halogens can be conveniently accomplished in a rather wide (say 2 cm.) test-tube in which a liquid can be boiled without loss from bumping. The whole analysis does not take more than ten minutes. The reagents used are neutral potassium iodate of one-tenth, potassium iodide of one-fifth, and nitric acid of five times molar concentration. (Specific gravity of the nitric acid = 1.18.) The procedure is the following:

(a) To the neutral solution add potassium iodate and acidify with acetic acid. Coloration shows the presence of iodide, which may be confirmed by shaking a portion with chloroform or carbon disulphide.

¹ *Loc. cit.*, p. 359.

(b) If iodide is found, add a little more potassium iodate to the main portion of the solution and boil. Repeat this procedure until further addition of iodate fails to produce coloration, but avoid more than a slight excess of iodate. Having expelled the liberated iodine by boiling, add to the solution nearly one-half its volume of dilute nitric acid. Coloration shows bromide, which may be confirmed by shaking a portion with chloroform or carbon disulphide.

(c) Boil the main portion of the solution until colorless, add 1 or 2 cc. of potassium iodide and boil again until colorless. The potassium iodide reduces the excess of iodate and the excess of iodide added is destroyed by the nitric acid. Boil again until perfectly colorless, then add an equal volume of concentrated nitric acid and a few drops of silver nitrate. A white precipitate, insoluble on warming, shows chloride. The concentrated nitric acid is added to prevent the precipitation of silver iodate in case there should still be some iodic acid left in the solution after the treatment with potassium iodide.

If sulphocyanate is present, the test for iodide must be made in a small portion of the solution after addition of sodium acetate. (We add an equal volume of the normal solution of the acetate.) The main portion of the solution is treated as above, the sulphocyanic and hydriodic acids being both completely oxidized in the presence of the acetic acid.

If salts of other acids are present, acidify the solution with dilute nitric acid and precipitate with silver nitrate. Digest the washed precipitate with zinc and dilute sulphuric acid. The halogen acids and sulphocyanic acid are thus brought into solution. Neutralize the solution, filter off the precipitate of zinc hydroxide or carbonate and proceed as directed above.

We have made some comparisons of the delicacy of this method for the detection of chlorides in presence of bromides and iodides with that of the commonly employed chromyl chloride distillation method. The limit of the latter method was found to be the detection of chloride in a mixture of 5 cc. N/100 sodium chloride with 10 cc. N/100 potassium bromide. With such a solution, a very faint yellow ring could be recognized at the top of the liquid (ammonium hydroxide solution) in the receiver. With less than 5 cc. of the sodium chloride solution, we failed to obtain any test

by this method, whereas, using our method, we were able to detect chlorine in mixtures of 0.5 cc. N/100 sodium chloride with 20 cc. of N/5 potassium bromide and iodide. In fact, the results of all our qualitative experiments indicate that absolutely no loss of chlorine is suffered in liberating and expelling the iodine and bromine.

To test the adequacy of the above directions we have had first- and second-year students of the University of Cincinnati analyze some forty mixtures of chlorides, bromides, iodides and sulphocyanates. The solutions were of fifth-normal to normal strength. In the reports there was but a single error, one student reporting chlorine when none was present. Some twenty-five mixtures of more dilute solutions, some containing as low as 0.5 cc. of the N/100 solution of one or other of the halide salts, many containing sulphocyanate and some containing salts of other acids, including reducing agents, such as sulphites, ferrocyanides, oxalates, etc., were analyzed by more experienced persons without error.

Bugarszky¹ has employed potassium biiodate and dilute sulphuric acid for the quantitative separation of bromine and chlorine but has not attempted to separate iodine from the other halogen elements. We hope soon to be able to communicate a method for the estimation of all three elements.

THE TESTING OF COAL TAR AND OILS AND AN IMPROVED TESTING STILL.

BY H. W. JAYNE.

Received June 4, 1903.

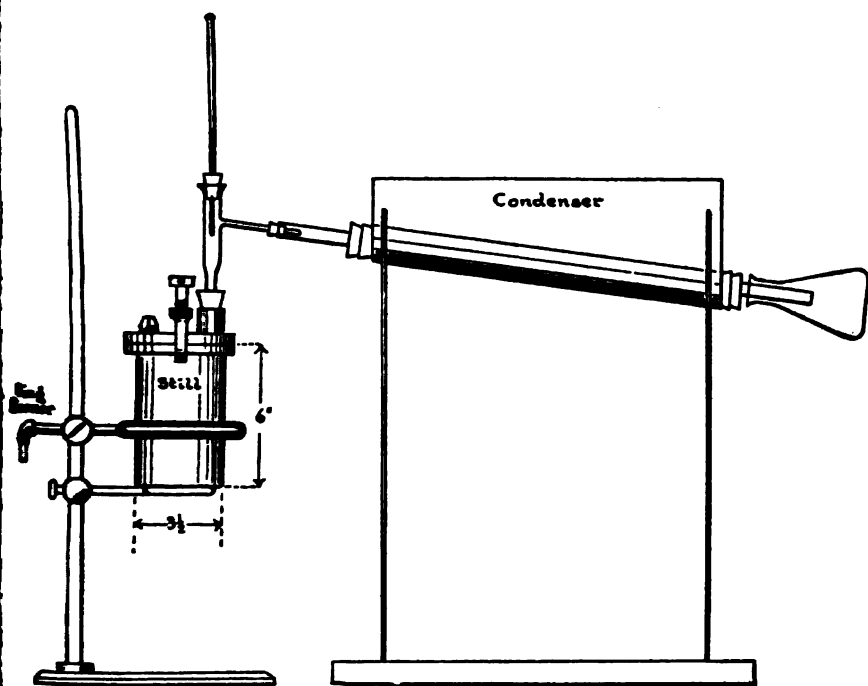
IN the examination of coal tars and oils, and in determining the per cent. of water they contain, it is necessary to distil a considerable quantity of material, from 500 to 1000 cc. at least. In treatises on this subject, it is usual to recommend the use of glass retorts of several liters capacity. As the temperature in making a complete test often rises to 400° C., and as water is usually present, the risk of breakage is very great; and when the distillation is finished, it is impossible to remove the pitch or residue completely.

In our laboratory, where hundreds of these tests are made every

¹ *Ztschr. anorg. Chem.*, 10, 387 (1895).

year, we found it necessary to substitute a metal still, and, in the course of time, improvements have been suggested by the different chemists making these tests, until a form of still and condenser has been adopted, which will be found convenient for those engaged in this line of work.

The still is of heavy copper with straight sides so that it can be easily and thoroughly cleaned. The upper edge is surrounded



with a heavy turned ring. The lid is of brass, and is clamped to the still by a single clamp passing over the top, a paper gasket being placed between the two metal surfaces. The condenser consists of a copper trough open at the top, through which passes a glass tube 24 inches long. This form of condenser is particularly advantageous for tar distillations. It is filled with water at the beginning of the test, and this is sufficient to condense all the lighter portions. When the fractions containing naphthalene begin to distil, they are liable to choke the tube by the crystallizing of this body. To prevent this, a burner is placed under the trough

and the water warmed to any degree required. When still higher temperatures are reached, where water cannot be used owing to danger of cracking the tube, it can readily be drawn off by the small cock.

In cases where it is necessary to distil very volatile liquids, pieces of ice or a freezing-mixture may be placed in the trough.

For oil-testing, the long Liebig condenser is not advantageous: it is difficult to clean; and on account of its length, considerable material adheres to the sides. As all tests of oils, naphthas and benzenes are run slowly, so that the distillate flows from the condenser in single drops, a long tube and flowing water is unnecessary.

One filling of water will suffice for many tests of benzenes or oils. If, however, flowing water is needed, the condenser is fitted with connections for tubing.

For water determinations, a small still is used of a capacity of 1000 cc. sufficient for distilling 500 cc. of tar. For complete tests of tars, especially if the light oils are to be examined, 1000 cc. should be used, and the still has a total capacity of 2000 cc.

For water determinations, great care must be taken in collecting the sample. If the shipment is made in bulk, a small cock should be placed in the pipe line from the car or boat to the tanks, and a small stream allowed to flow during the entire pumping. The quantity so collected should be violently stirred, and at once filled into wide-mouthed quart bottles or cans before any separation can take place. 500 cc. of this sample are filled into the still, the lid securely clamped, and the tube and thermometer put in place. If heat is applied to the bottom of the still, great care must be used, as the contents will readily foam and boil over, if much water is present; this is especially true of tars containing much free carbon along with water, and also of certain oil tars in which the water forms an emulsion.

To avoid this, a ring burner is provided which surrounds the still, and is at first placed so that the heat strikes about the top of the tar in the still. Little attention need be given the distillation but from time to time the ring burner is lowered, until finally nearly all the water is driven out, when, if necessary, an additional burner is placed under the bottom.

In order to be certain that all water is expelled, the temperature of the thermometer in the vapor should reach 200°C . As the distillation proceeds, oil comes over with the water until at 200° a considerable quantity of the former has distilled. The volume of the water is then read off in cubic centimeters, and gives the volume per cent., on which all these tests are based.

If, after the water has been determined, it is desired to examine the tar or oil further, the oil which has distilled over with the water is carefully separated from the latter and added to the cooled tar in the still, and the distillation recommenced; thus, the subsequent determination will be based on dry tar. Unless this is done, false results are obtained, due to the oils distilling at lower temperatures in the presence of vapor of water. For example, a tar, which, if dry, would show 5 per cent. distilling under 200°C ., might show 20 per cent. to the same point if much water was present.

The ring burner may be dispensed with during this latter distillation, and it is advisable to cover the still with a sheet of asbestos, if a high temperature is to be finally reached.

If at any time it is desired to examine the material in the still, this can be done without dismounting the apparatus by removing the small plug in the lid, and introducing a rod. The pitch or residue can be tested as to the melting-point or other properties, and if not of the desired test, the distillation can be continued.

Some tars are exceedingly difficult to free from water, the contents of the still boiling over notwithstanding all precautions. If it is desired to determine only the water in these, the removal of the latter can be greatly facilitated by adding to the tar a hydrocarbon, boiling slightly higher than water—crude or refined toluene, for instance. This thins the tar, and as it distils readily, carries over the water completely. Distillations which otherwise would require hours to complete, can be then readily made in twenty minutes.

This method is also very advantageous for determining water in naphthalene or oils rich in this substance, as it facilitates the driving out of the last traces of water, and prevents crystallizing of the naphthalene in the condenser tube and receiver, and permits the volume of water to be readily read off.

In these determinations a pure product need not be used—any hydrocarbon boiling between 100° and 200° will serve, the precaution being taken, however, to determine how much water it contains, and allowing for the same.

Recently a German patent No. 130,295 was granted for determining water in substances by adding a higher boiling liquid than water and one that does not mix with it. It is to be regretted that these simple laboratory methods should be made the subjects of patents, and it is difficult to understand the object of taking such a patent; but in this case it would be invalid in the United States, as the method has been used for a long time at different works.

LABORATORY, BARRETT MANUFACTURING CO.

A PROCESS FOR MAKING AVAILABLE PHOSPHATES.

BY C. H. DEMPWOLF, JR.

Received May 29, 1903.

A NUMBER of processes for the manufacture of available phosphates by means other than that of sulphuric acid have been recently proposed. From among these processes the following have been taken as seeming of the most importance.

G. F. Wilson (1861) patented a process, which consists in treating ground mineral phosphates, bone-black, etc., with fused sodium bisulphate and steam under high pressure. A double decomposition of the tricalcium phosphate into calcium sulphate and sodium phosphate is claimed for the process, thus leaving the phosphoric acid in a form more available as a plant food. The source of the bisulphate is the waste product obtained in the manufacture of sulphuric and hydrochloric acids.¹

G. A. Liebig (1881) proposed a process in which phosphates are mixed with carbon and subjected to a high heat. The proportions given are two parts of the phosphate to one of carbon.²

The process of Brunner and Zanner consists in treating the finely powdered natural phosphates with a solution of sodium bisulphate. After filtration, the liquid contains the calcium acid phosphate, which is then precipitated by an excess of lime.³

¹ U. S. Patent 75,325.

² U. S. Patent 241,868.

³ *Moniteur Scientifique*, 1892, p. 100, and Eng. Patent 2,389, Feb. 8, 1892.

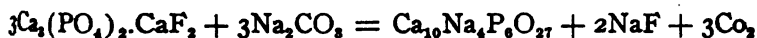
A method of making hydrated phosphate of alumina soluble in ammonium citrate was proposed by Pillon Freres and Buffet in 1892. This process is simply a dehydration by the action of heat and is used in the manufacture of Redonda phosphate.¹

Stephen L. Goodale obtained a United States patent on a similar process in 1893. Morse has shown, however, that the dehydrated phosphate of alumina, as sold under the name of Redonda phosphate, absorbs water very rapidly and reverts to the hydrated or insoluble form, this being its probable action in the soil.²

C. H. Knoop, by heating mixtures of natural phosphates with alkaline silicates or materials capable of forming these silicates, to a red heat, obtained a complex alkaline phosphate, in which 99 per cent. of the phosphoric acid is soluble in Wagner's citrate solution. The following charges are given as yielding good results:³

	Parts.
Tricalcium phosphate	100
Calcium carbonate	80
Sodium sulphate.....	60
Silica	54
Tricalcium phosphate.....	100
Calcium carbonate.....	36
Magnesium sulphate.....	185
Silica	54

J. G. Wiborgh, of Stockholm, obtained a patent in the United States on a process of igniting apatite with alkaline carbonates or hydroxides. It consists in pulverizing the apatite and mixing it with carbonate of sodium or potassium or with sodium or potassium hydroxides, and subsequently heating the mixture to a red or yellow heat. A tetracalcium sodium (or potassium) phosphate is formed according to the following equation:



This double phosphate is readily soluble in ammonium citrate.⁴

A more recent patent of Wiborgh and Palmaer (1903) describes an electrolytic process for the manufacture of soluble phosphates. Apatite or other phosphate is placed in an electrolytic cell with a salt solution adapted to liberate an acid at the anode, forming a soluble salt with lime, while at the cathode a basic hydroxide is

¹ *Moniteur Scientifique*, 1892, p. 210, and Eng. Patent 6,023, Nov. 30, 1892.

² *This Journal*, 1903, p. 280.

³ *Centralblatt*, 1899, p. 1052.

⁴ U. S. Patent 601,069.

formed, the acid dissolving the phosphate and precipitating the same in the alkaline liquid of the cathode.¹

Shutt, in a paper on the action of ground mineral phosphates as a fertilizer,² describes experiments on the fusion of apatite with sodium sulphate and sodium bisulphate. It was found that when apatite is fused with sodium sulphate, 35 per cent. of the total phosphoric acid in the product becomes soluble in a 2 per cent. citric acid solution. When the bisulphate is used, 50 per cent. of the total phosphoric acid is soluble.

The use of a 1 per cent. citric acid solution as a means of determining the availability of phosphates as a plant food is customary in England. The results obtained by Shutt are probably higher than would be given by a 1 per cent. citric acid solution or the neutral solution of ammonium citrate, as adopted by the Association of Official Agricultural Chemists.

Baskerville noted that when natural phosphates were heated with alkaline salts, such as sodium sulphide, sodium nitrate, sodium carbonate and sodium sulphate, a large proportion of the phosphoric acid became citrate-soluble. The rock contained 35 per cent. $\text{Ca}_3(\text{PO}_4)_2$ and was mixed with sodium carbonate in the proportion of 4 of rock to 1 of carbonate. The mixture was heated to a red heat and gave a 75 to 90 per cent. yield, depending upon the temperature and the duration of heating. The percentage of water-soluble phosphoric acid was not notably increased.³

EXPERIMENTAL.

This work was undertaken with a view to the utilization of niter cake, the by-product from the manufacture of sulphuric acid, and at the same time the production of an available phosphate. This niter cake is the residue from the treatment of sodium nitrate with sulphuric acid and is composed mainly of sodium bisulphate with a small percentage of the normal sulphate. The niter cake used in these experiments was found to contain NaHSO_4 , 86.93 per cent.; Na_2SO_4 , 9.72 per cent.

EXPERIMENTS WITH BONE ASH.

Twenty grams of ground bone-ash containing 40.16 per cent. insoluble phosphoric acid was mixed with an equal quantity of niter cake and heated in a porcelain crucible for thirty minutes

¹ U. S. Patent 707,886 and this Journal, 1903.

² *Chem. News* (1896), p. 4.

³ *J. Soc. Chem. Ind.*, December, 1902.

with the blast-lamp. The mixture before heating contained 20.08 per cent. phosphoric acid. A second charge was run at the same time, using 20 grams bone-ash, and 20 grams niter cake, with the addition of 4 grams charcoal. This mixture was heated for the same length of time and at the same temperature as in the first case.

The analyses of the sintered masses may be stated as follows:¹

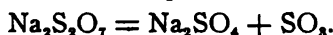
Charges.	20 grams bone-ash. 20 grams niter cake.	20 grams bone-ash. 20 grams niter cake. 4 grams carbon.
Water-soluble P_2O_5	0.13	3.70
Citrate-soluble P_2O_5	2.66	14.16
Insoluble P_2O_5	18.30	6.59
Total P_2O_5	20.99	24.45
Ratio of available P_2O_5 to total P_2O_5 ..	13.24	73.05

This increase in the percentage of available phosphoric acid is due mainly to the formation of the double phosphate of calcium and sodium ($Ca_{10}Na_4P_6O_{27}$), which is soluble in ammonium citrate solution and to a slight extent to the fact that tricalcium phosphate is more soluble in water containing alkaline salts than in pure water. Other double phosphates of calcium and sodium have been prepared, and Baer mentions a calcium sodium pyrophosphate having the formula $CaNa_2P_2O_7 \cdot 4H_2O$.² The formula as given by Wiborgh corresponds to the tetracalcium phosphate as present in basic or Thomas slag and is probably the one which is formed under these conditions.

The analyses show that when carbon was used, the ratio of available phosphoric acid to total phosphoric acid was increased from 13.24 to 73.05 per cent. The sodium bisulphate was used in excess over the amount necessary to form the double salt $Ca_{10}Na_4P_6O_{27}$, while the carbon used was the calculated amount necessary to reduce the sodium acid sulphate to sodium sulphide. When sodium bisulphate is heated, it loses water according to the equation



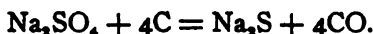
This pyrosulphate, at a somewhat higher temperature, loses sulphur trioxide and the normal sulphate is formed,



¹ The methods of analysis used in these experiments were those adopted by the Association of Official Agricultural Chemists and described in Wiley's "Principles and Practice of Agricultural Analysis," Vol. II.

² Pogg. Ann., 75, p. 159.

The action of the carbon is to reduce the normal sulphate thus formed to sodium sulphide according to the following reaction:



It is probable that some polysulphides are also formed.

EXPERIMENTS' WITH PHOSPHATE ROCK.

Similar experiments were made, using a natural Florida phosphate containing 30.28 per cent. P_2O_5 , of which 1.30 per cent. was citrate-soluble. These charges were heated exactly as in the preceding case and yielded the following analyses:

Charges.	30 grams rock. 20 grams niter cake.	20 grams rock. 20 grams niter cake. 4 grams carbon.
Water-soluble P_2O_5	0.38	0.27
Citrate-soluble P_2O_5	5.12	8.87
Insoluble P_2O_5	13.89	11.55
Total P_2O_5	19.39	20.69
Ratio of available P_2O_5 in total P_2O_5 ..	28.36	44.17

Here the increase in yield, due to the action of the carbon in forming sodium sulphide, is not so large as when bone-ash was used.

The effect of heat alone upon the phosphate rock was determined by igniting 20 grams of the rock for thirty minutes in the blast. The analysis, after ignition, shows a small increase of citrate-soluble phosphoric acid, due probably to the dehydration of the ferric and aluminum phosphates present.

	Analysis of rock before ignition.	Analysis of rock after ignition.
Total P_2O_5	30.28	31.82
Citrate-soluble P_2O_5	1.30	3.27

A mixture of 10 grams phosphate rock and 10 grams sodium sulphide, heated as described above, gave the following analysis:

Water-soluble P_2O_5	0.18
Citrate-soluble P_2O_5	11.32
Insoluble P_2O_5	8.86
Total P_2O_5	20.36
Ratio of available P_2O_5 to total P_2O_5	56.43

It was believed that the above results could be improved upon, and the following experiments were made in order to determine the effect of temperature, duration of heating and the proportion of ingredients in the mixture upon the amount of available phosphoric acid in the product.

In order to determine the most effective temperature, mixtures of 10 grams phosphate rock, 10 grams niter cake and 2 grams charcoal were heated for thirty minutes at temperatures of 830°, 1090° and 1200° C. and for one hour at 830° and 1090° C. The analysis of the products are shown in the following table:

	30 minutes.			1 hour.	
Temperature	830°	1090°	1200°	830°	1090°
Water-soluble P_2O_5	0.16	0.33	0.24	0.30	0.25
Citrate-soluble P_2O_5	8.26	10.00	12.55	8.19	13.57
Insoluble P_2O_5	11.83	9.54	8.77	12.05	7.33
Total P_2O_5	20.25	19.87	21.56	20.54	21.15
Ratio of available P_2O_5 to total P_2O_5	41.58	51.98	59.32	41.33	65.34

These results indicate that the amount of available phosphoric acid is increased by an increase in temperature and duration of heating. The charges heated to 830° and 1090° were very porous and easily pulverized, while the charge heated to 1200° for thirty minutes was partly fused and difficult to break.

Mixtures containing 10 grams phosphate rock and varying proportions of 4, 6, 8 and 10 grams niter cake, with carbon sufficient in each case to reduce the bisulphate, were made up and heated for one hour at a temperature of 1090° C. The results of the analyses of these products are as follows:

	10 grams rock. 4 grams niter cake. 0.8 gram carbon.	10 grams rock. 6 grams niter cake. 1.2 grams carbon.	10 grams rock. 8 grams niter cake. 1.6 grams carbon.	10 grams rock. 10 grams niter cake. 2 grams carbon.
Water-soluble P_2O_5	0.12	0.19	0.28	0.25
Citrate-soluble P_2O_5	16.53	15.74	12.53	13.57
Insoluble P_2O_5	10.84	9.13	8.96	7.33
Total P_2O_5	27.49	25.06	21.77	21.15
Ratio of available P_2O_5 to total P_2O_5	60.56	63.56	58.84	65.34

The differences shown above between the ratios of available phosphoric acid to total phosphoric acid are not very great, the best yield being obtained with the mixture containing 10, 10 and 2 parts respectively of rock, niter cake and carbon. The product from this charge contained considerable excess of sodium sulphide, which, on exposure to air, oxidized to sulphate and absorbed water very rapidly. One gram of this phosphate was exposed under a bell-jar for several days to an atmosphere saturated

with moisture. The increase in weight due to oxidation and absorption of water was noted as follows: After 24 hours, 0.1856 gram; after 48 hours, 0.2148 gram; after 72 hours, 0.2254 gram.

One gram of the phosphate from the mixture 10 grams rock, 4 grams niter cake and 0.8 gram carbon was exposed in a similar manner, the absorption in this case being considerably less than the above figures. The increase in weight for three days was after 24 hours, 0.0384 gram; after 48 hours, 0.0522 gram; after 72 hours, 0.0550 gram.

A modification of Knoop's charge, using a proportional quantity of niter cake in place of the normal sodium sulphate, was tried, but with little success. The charge was made up by mixing 20 grams phosphate rock, 10.6 grams calcium carbonate, 16 grams niter cake and 6.6 grams silica, and heated for a half hour at a temperature of 1090° C.

Analysis:

Water-soluble P_2O_5
Citrate-soluble P_2O_5	0.80
Insoluble P_2O_5	12.31
Total P_2O_5	13.11
Ratio of available P_2O_5 to total P_2O_5	6.10

A double phosphate and silicate of lime corresponding to the formula $Ca_3(PO_4)_2 \cdot CaSiO_4$ would be formed under these conditions and does not seem to be soluble to any great extent in the neutral citrate of ammonia.

A method of treating the phosphate rock with the niter cake in solution was more successful than any of the above-described experiments. Twenty grams of the ground rock and twenty grams of niter cake were mixed in a beaker-glass and water added to form a thin paste. This was allowed to stand for four weeks with frequent addition of water and stirring, at the end of which time the water was allowed to evaporate and the mixture dried in the air. An analysis of the product thus obtained was as follows:

Water-soluble P_2O_5	6.89
Citrate-soluble P_2O_5
Insoluble P_2O_5	5.54
Total P_2O_5	12.43
Ratio of available P_2O_5 to total P_2O_5	55.43

In this case no citrate-soluble phosphoric acid was formed, all of the available phosphate being soluble in water. The tricalcium phosphate, being somewhat soluble in water containing alkaline salts, neutralizes the acidity of the bisulphate according to the equation



CONCLUSIONS.

The sulphuric acid industry being so closely allied to the manufacture of fertilizers, it would seem from the foregoing work that it is possible to utilize the sodium bisulphate, niter cake, to good effect in the production of an available phosphate. The cost of producing acid phosphate on a large scale by means of sulphuric acid is very low and any process, even though an auxiliary one, for the production of the same phosphate must necessarily be a cheap one.² The method of heating mixtures of niter cake, phosphate rock and carbon would probably be more expensive than the present one for any but a cheap low-grade phosphate rock. Furthermore, there is a general prejudice against the use of citrate-soluble or so-called "reverted phosphoric acid", although it has been given the same value as that soluble in water by the various experiment stations of this country.

It is believed by agricultural chemists that when an acid phosphate, containing the various forms of phosphoric acid is applied to a soil containing iron and alumina, the soluble parts of the compound tend to become fixed by union with such bases or by precipitation as $\text{Ca}_2\text{H}_2(\text{PO}_4)_2$.³

The method of treating the pulverized phosphate with a solution of niter cake promises to be more successful, since the available phosphoric acid in the product constitutes 55.43 per cent. of the total phosphoric acid and is completely soluble in water. By finer grinding of the rock, it may be possible to increase the yield, and the time four weeks may be longer than is necessary to complete the reaction.

¹ It is possible that some sodium phosphate may be formed in the above process.

² A 14 per cent. acid phosphate can be made for about \$7 per ton.

³ Wiley's "Principles and Practice of Agricultural Chemical Analysis," Vol. II., p. 140.

A PRELIMINARY REPORT UPON THE OXIDATION OF LINSEED OIL.

BY FREDERICK L. DUNLAP AND FRANCIS D. SHENK.

Received May 21, 1903.

The question of the phenomenon of the drying of linseed oil is one of great interest, but while more or less work has been done on this subject, in order to elucidate the chemical changes taking place during the drying of linseed as well as other drying oils, yet our knowledge of the subject is far from complete. We undertook this work with the hope of being able to throw more light on this question, but the fact that we are unable to further carry on this work in conjunction, makes it necessary that this report should be considered merely in the light of a preliminary one, and it is hoped that later, one of us may be able to fill in the gaps that are lacking in the experimental part of this report.

The first work of importance on the subject of the chemistry of drying oils, with reference to the action of air on them, is in the classic work of Mulder,¹ although previous to Mulder, Unverdorben² and Leuchs³ had made a brief study of the action of air on linseed oil, but their results were not such as to lead to any definite conclusions.

Mulder's work on the chemistry of the drying oils, was published in German in 1867, and included in it the results of his researches on the action of air on linseed oil as well as on the free acids of linseed oil. At the time when Mulder carried on his researches, the knowledge of the constitution of these oils was very incomplete, nor was much known about them until the publication of the beautiful researches of Hazura and others in the *Monatshefte*.⁴ Mulder came to the conclusion that the liquid acids in linseed oil contained besides oleic acid, an acid of the composition $C_{16}H_{28}O_2$ (leinölsäure). On oxidation of linseed oil by means of air, Mulder held that the glycerin was completely oxidized, that the free fatty acids and the greater part of the oleic acid remained unchanged, and that the acid $C_{16}H_{28}O_2$ at first formed the acid $C_{16}H_{26}O_6$ (linoxysäure) and finally as an end-product of the oxidation, the neutral linoxyn $C_{32}H_{54}O_{11}$.

¹ "Chemie der austrocknenden Oele." Translated from the Dutch by J. Müller. Berlin, 1867. Julius Springer.

² Schweigger's *Jour.*, 17, 245.

³ Gmelin-Kraut, 7, 1231.

⁴ 7, 216; 8, 147, 156, 260; 9, 180, 198, 475.

Hazura¹ has shown as the results of his study of the action of potassium permanganate on an alkaline solution of the liquid acids of linseed oil, that linseed oil contains the glycerides of the following acids: Oleic, $C_{18}H_{34}O_2$; Linolic, $C_{18}H_{32}O_2$; Linolenic, $C_{18}H_{30}O_2$; Isolinenic, $C_{18}H_{30}O_2$. It was impossible that Mulder should have been able to come to any correct conclusion on the oxidation of linseed oil by means of air, for from the work of Hazura we can see that Mulder was dealing with a more complicated product than he was aware of, and that,² for example, his linoxy acid, $C_{18}H_{30}O_3$, obtained from the acid $C_{18}H_{32}O_2$, could not have been the simple product that Mulder took it to be, but must have been a mixture of products, which furthermore could not have contained an acid of the chain C_{18} , but must have been those of the higher chain C_{19} .

Bauer and Hazura³ studied the phenomenon of the drying of oils, and have clearly shown that the results obtained by Mulder on his linoxy acid are unreliable. So far as the action of air is concerned, Bauer and Hazura studied its action on the free acids of linseed oil, on the barium and lead salts, and on the linseed oil itself. In brief, their conclusions are as follows: The oleic acid undergoes no change whatsoever; the more linolenic acid there is in the oil, the more rapidly it dries; the oxidation consists not only in the saturation of the free valencies with oxygen, but also in the formation of compounds containing hydroxyl groups; the acids dry, on long exposure to the air, with the formation of anhydrides, but that they were unable to say whether such anhydrides were lactonic in nature or formed from 2 molecules of the oxyacids; and finally, that there is no difference between the drying of the free acids and their salts.

For some not very well-defined reason, Bauer and Hazura concluded that as they had shown clearly the constitution of the unsaturated acids in linseed oil, it appeared "unnecessary to isolate the individual compounds from the oxidation product obtained from the acids of linseed oil by the action of air upon them; it is sufficient to show in what way the oxidation takes place." In this, we can not agree with Bauer and Hazura that all that is necessary is to show in what way the oxidation takes place, unless

¹ *Monatsh. Chem.*, 9, 191 (1888).

² *Ibid.*, 9, 460 (1888).

³ *Ibid.*, p. 459, et seq.

in so doing, it is perfectly evident what the final products of such an oxidation may be. In order to elucidate the chemical changes taking place when linseed and other oils dry, either the individual oxidation products must be isolated and analyzed, or else, if this prove impracticable, results must be obtained from some other but less direct route. None of the experimental results of Bauer and Hazura can be interpreted to mean that the oxidation by air gives rise to the same products as are obtained by the action of potassium permanganate on an alkaline solution of the linseed oil acids. Nor are the conclusions of Bauer and Hazura as given above, namely, with reference to the formation of hydroxy acids and anhydrides, etc., given with sufficient definiteness to help us to anything like a clear understanding of the question. We have spent considerable time in attempts to isolate some of the hydroxy acids described by Hazura¹ as resulting from the action of potassium permanganate on the unsaturated acids of linseed oil, but, in the product obtained from the action of air on linseed oil, we have been unable to obtain a trace of any product resembling those obtained by Hazura with potassium permanganate, nor is there any *a priori* reason for believing that the oxidation would follow the same lines. We judge from the context of the article of Bauer and Hazura that they wish to convey the idea that air and potassium permanganate produce identical results in the oxidation in question, otherwise we are at a loss to understand why they deem it unnecessary to isolate the oxidation products, but think it sufficient to dismiss the question with a few conclusions quoted at the beginning of this paper.

In 1893, Fahrion² published an article on the oxidation of oils by means of air, in which work he gives the results of some oxidation products which he isolated and subjected to analysis. He oxidized linseed oil, for example, by saturating chamois skin with the oil and allowing the skin so treated to hang in the air until the oxidation was finished. But Fahrion himself shows that he had not obtained pure products, but only mixtures of various oxy-acids.

The above references to the literature give, so far as we have found, the results bearing directly on the chemical changes taking place during the drying of linseed oil.

¹ *Monatsh. Chem.*, 9, 191 (1888).

² *Chem. Ztg.*, 17 (2), 1849 (1893).

We have attacked the problem in two ways, first, the oxidation of linseed oil when dissolved in ligroin; and second, when dissolved in benzene. A reference to the action of air on linseed oil, when dissolved in benzene, occurs in Allen's "Commercial Organic Analysis."¹ Whether this work is abstracted from a published article or is the result of some experiments carried out by Allen himself, we cannot say, but we have found no trace of any suggestion regarding the oxidation of linseed oil in benzene solution other than that given by Allen. The few lines devoted by Allen to this subject, do not contain any results which cast any light on the chemical side of this phenomenon of oxidation.

The serious objection to the oxidation of linseed oil by spreading it in thin layers on metal or glass plates, and then exposing them to the air, either at ordinary or elevated temperatures, is that it is a process that may take weeks or even months of exposure in order to bring about thorough oxidation, and even then it is a serious question whether or not the oxidation has become complete. As soon as the superficial layer of the oil becomes coated with a layer or film of the oxidized product, the oil lying below this film, and which is unacted upon by the air, is more or less effectively removed from the action of the air by the film on the surface. This latter objection is also applicable to Fahrion's scheme of oxidizing linseed oil which has been exposed to the air on chamois skin.

By dissolving the linseed oil in a suitable solvent, and then aspirating air through it, the above objections are readily overcome. Low-boiling ligroin and benzene serve admirably for this purpose.

The sample of linseed oils used for the experimental part of this work, was a sample of pure boiled oil containing lead and manganese as driers. The iodine number, acid value, etc., of this oil, are given at the beginning of the table later on in this article.

To determine the rate of oxidation, 100 grams of the boiled oil were dissolved in 1,000 cc. of ligroin (boiling-point below 90°) and air drawn through the solution. This was started November 10th. After forty-eight hours, the oxidation product that had separated was filtered off, thoroughly macerated with ligroin, then

¹ Third edition, Vol. II, Part I, p. 152.

washed several times with a lower boiling product to remove any of the original linseed oil mechanically held. After drying first in air then *in vacuo* over sulphuric acid, a sharp odor was given off similar to that of hydrochloric acid, only stronger, and resembled the odor of acrolein. This solid oxidation product weighed 17.5 grams. Air was again drawn through the ligroin solution and after forty-eight hours more, a second batch was filtered off. This also had the sharp odor noted above. This lot weighed 24 grams. A third lot was taken out November 16th ; weight, 25 grams. It did not have the sharp odor—was white and almost transparent. The fourth and last batch was filtered off four days later; it weighed about 15 grams and looked the same as the third lot. Air was again drawn through the solution until November 24th, and as no product had separated since the last filtering, it was sufficient evidence that the oxidation was complete November 20th or before. The total weight of products was 81.5 grams. The remaining solution was clear but fluorescent while cold, and upon distilling off the ligroin *in vacuo*, the fluorescence disappeared and a precipitate formed. Weight of final product was 20 grams. The ligroin that distilled off had a very sharp penetrating odor like that previously mentioned in connection with the first oxidation products. After standing for a couple of weeks, the sharp odor entirely disappeared from the ligroin. About 5 grams of the last product was solid, the rest a deep yellow oil. The first oxidation products that separated were darker in color than those separated later. During the aspirating of air through the ligroin solution of the linseed oil, the ligroin lost by evaporation was replaced by fresh solvent so that the volume remained practically constant.

Since the oxidized oil seemed to form two distinct products, so far as color was concerned, an experiment was run to determine whether there was any special difference between them. This was started in the same way as the above experiment, but the oxidation product was allowed to collect until the oxidation was complete. A mechanical separation was then made of these two layers. The dark layer, called A, and the light layer, called B, were each subjected to the method of washing previously mentioned. Each layer weighed approximately 60 grams. They were then sub-

jected to repeated extractions with boiling ether until no residue remained on evaporating the solvent. The ether extract from A (A_1) weighed 20 grams, while that from B (B_1) weighed 30. As will be seen from the following table, there is a slight difference in the iodine numbers of the ether-soluble and the ether-insoluble portions of the product A. The part A carried more of the manganese of the dryer than the part B.

The ether insoluble of B was extracted several times with large quantities of boiling chloroform. Out of 31 grams taken, only 28 grams were dissolved by the chloroform; this, after evaporating off the solvent, was of a reddish brown color, but gradually turned white on standing. The part insoluble in chloroform was a grayish white product of a rubbery consistency. According to Mulder¹ the oxidation product is dissolved by a mixture of alcohol and chloroform, but the products we obtained were not, if conclusions can be drawn from the following experiment. Four-tenths of a gram of the ether-insoluble portion was heated to boiling for sixty hours in a mixture of 400 cc. of alcohol and chloroform, one part of the former to four of the latter. At the end of that time a considerable portion was still undissolved. When heated with alcohol and chloroform, the product does swell, but the swelling is due to the chloroform alone, not to the alcohol. It also swells slightly when heated with ether and can be easily ground to a fine powder after the ether is poured off.

On December 5th another sample of 100 grams of the oil was oxidized as the above, but benzene was used instead of ligroin. At first, no product separated as from the ligroin solution. At the end of eighteen days the oil had an iodine number of 37; by January 15th the iodine number was 24.9. By February 1st a solid product had separated out; this was filtered off and washed several times with benzene. The dry product, called C, weighed 18 grams. Air was again drawn through the remaining oil for a month more, but nothing further separated. After filtering off the solid product, the oil had an iodine number of 35, and the lowest we were able to get it after that was 31. Twenty-two per cent. of the above solid product was soluble in ether, which shows that the product may differ to a certain extent from that separating from the

¹ "Chemie der Austrocknenden Oele," p. 98.

ligroin, as the ether-soluble part of the product separating from ligroin was nearly 50 per cent. of the total solid.

In determining the iodine number, the various samples had to be heated to the temperature of the water-bath in order to effect solution (except in the case of the ether-soluble). When this had been accomplished, Wiji's solution of ICl in glacial acetic acid was added and allowed to stand for lengths of time varying from fifteen minutes to nearly an hour. In general, the iodine absorption was found to be complete in twenty-five to thirty-five minutes, *i. e.*, for a shorter time the iodine absorption was low and increased to a constant when allowed to stand for the period just indicated.

The dissolving of the oxidation product in glacial acetic acid, by means of heat, produced a solution of slightly reddish color. Where, for example, the product was soluble on long shaking with glacial acetic acid at ordinary temperatures, as were the ether-soluble products A₁, B₁ and C₁, the iodine absorption was found to be less than when such solution was effected by means of heat. For the ether-soluble products A₁, B₁ and C₁, solution was effected by means of automatic shaking for periods varying from three to ten hours, and in the following table the iodine numbers given represent the results of solution produced without the aid of heat.

A₂ and B₂ were nearly all soluble in cold glacial acetic acid and it is highly probable that they are completely soluble if sufficient acid is used, but we were unable to carry out this work for lack of time.

A₁, B₁ and C₁ were all thick, viscous, yellowish oils, which on long standing in the air grew more viscous, becoming coated with a film like that forming on linseed oil itself. A₂, B₂ and C₂ were of a leathery or gutta percha-like consistency.

In determining the iodine numbers, Wiji's method was used throughout, as Hübl's method could not be used, for glacial acetic acid was found to be the only satisfactory solvent for these products.

The following table gives some of the results obtained from the various oxidation products.

Substance.	Iodine number.	Acid value of potassium hydroxide. Milligrams.	Saponification value of potassium hydroxide. Milligrams.	Ether value.
Original oil	{ 176.6 176.9	{ 4.00 4.00	{ 183.0 180.6	{ 177.8
A	{ 44.8 (?) 54.2	{	{	{
B	{ 26.7 28.5	{	{	{
C	{ 22.0 22.7	{	{	{
A ₁ , soluble in ether	{ 54.9 54.2	{ 64.5 64.7	{ 251.7 258.0	{ 190.2
B ₁ , soluble in ether	{ 42.2 42.1	{ 66.5 67.0	{ 237.2 239.1	{ 171.4
C ₁ , soluble in ether	{ 25.4 25.4	{ 98.2 101.1	{ 330.0	{ 230.4
A ₂ , insoluble in ether	{ 32.5 34.8	{	{	{
B ₂ , CHCl ₃ extract of ether-insol. .	{ 32.2 32.9	{ 71.2 } ₁ 85.7	{ 321.1 322.3	{ 243.3
C ₂ , insoluble in ether	{ 24.2 24.7	{	{	{
B ₃ , insoluble in ether or CHCl ₃ .	{ 28.6 29.1	{	{	{
Oil not precipitated from ligroin	{ 65.0 66.0	{ 21.6 21.7	{ 193.1 193.9	{ 171.4
Acids from ether-soluble. (B ₁)	{ 51.8 52.9	{ 231.2 231.5	{ 268.9 269.6	{ 37.7 ...
Acids from ether-insoluble. (B)	{ 43.4 45.9	{ 265.2 265.8	{ 307.0 309.0	{ 42.4 ...

The ether value was obtained by taking the difference between the mean of the saponification values and the mean of the acid values.

From the free fatty acids of A₁, B₁ and C₁ white crystalline products were obtained. Crystalline products of a similar nature were obtained from the ether-insoluble portion. To show that this product did not come from any of the original oil carried down mechanically by the oxidation product, 25 grams of the oxidized oil were heated with ether, which rendered the product very brittle, and it was then finely ground. This was then extracted with ether in a Soxhlet extractor for ten hours, which removed all of the original oil and also all of the oxidized part soluble in ether. When

¹ These figures do not represent the true acid value, as we found it impossible to bring the last traces of this product into solution, before titrating with potassium hydroxide.

the product was dried after the extraction, it was of the consistency of cornmeal, and absolutely free from sticky material. It required not over fifteen minutes for complete saponification with a 25 per cent. potassium hydroxide solution; sufficient heat was generated by the reaction itself to effect the result. The fatty acids were thrown out with sulphuric acid and the solution cooled with ice so the acids could be lifted out in a lump with a stirring rod; without cooling, the acids could not be separated from the water by mechanical means. They were then thoroughly washed with water and dried; the weight was 15.2 grams. After mixing with quartz sand, the acids were extracted with ligroin. The weight of product extracted was 1.2 grams. This was perfectly white and was crystallized from glacial acetic acid. The part insoluble in ligroin was then extracted with ether. The ether extract weighed 10 grams; that insoluble in ether weighed nearly 4 grams and was very dark in color.

By fractional crystallization, 1.2 grams of the white crystalline product were separated into two products melting at 60° - 61° and 52° - 53° . This required a large number of fractions to be made, and at the end of this work but very small amounts of the two products were obtained. We are disposed to think that these two products are respectively palmitic and myristic acids, although it is difficult to understand how these acids could have been present in the product from which they were obtained, for, as pointed out above, this product had been extracted for ten hours with ether.

The fact that the benzene solution of linseed oil could not be brought to have a lower iodine number than 31 by continued aspiration of air through the solution, shows conclusively that the products of which linseed oil is composed can not be completely oxidized by air. From what is known of oleic acid and its properties, there is no reason to doubt but that the iodine number was produced, at least in part, from the unchanged oleic acid or olein. This, however, is but in agreement with the well-known fact that oleic acid is practically unacted upon by the oxygen of the air. From the large increase in the acid value, it is evident that the oxidation of linseed oil by air takes place to a considerable extent through the oxidation of the glycerin of the glycerides. While we have been unable, for lack of time, to attempt an isolation of the product having the sharp, characteristic odor of acrolein, yet

it is not impossible that acrolein may be formed during this progress of oxidation. That the air oxidizes linseed oil with the formation of carbon dioxide, formic and acetic acids, has been shown by Mulder¹, from which we can see that the chemical changes taking place during the drying of the glycerides are complex. That the acrolein-like odor came from the linseed oil and not from the ligroin, was determined by a blank experiment. It is also evident that the oxidation in ligroin by means of air gives rise to products that are still unsaturated. While no acetyl values were determined, yet it was sufficiently well shown by Hazura² that products containing the hydroxyl group are formed. That we were, for example, dealing with a product free from any unoxidized oil or free oleic acid, let us consider such a product as B₁ or C₂. If any unoxidized oil was carried down mechanically with the oxidized product, it must have been in small quantities. If any such occluded oil or free oleic acid were present, it must have been completely removed by the subsequent maceration and washing of the product with ligroin, and in the long and thorough extraction with ether. Even after such treatment, the iodine number of C₂ was found to be 24.5 (mean value), while in the case of B₁ it was 33.6 (mean value), and in B₂ it was 28.9 (mean value). From this we must conclude that the oxidized product thrown out from a ligroin solution is an unsaturated hydroxylated product.

What the exact chemical nature of these products is, it is, at present, impossible to say; nor can we, as yet, be assured that the product obtained from ligroin is identical with the product obtained by oxidation without a solvent. Bauer and Hazura³ obtained, by Hübl's method, an iodine number of 28.8 and 29.4 for the free acids obtained from linoxyn. We obtained an iodine number of 43.4 and 45.9 from our corresponding product, *i. e.*, the free acids of the ether-insoluble portion.

The ether values 37.7 and 42.4, obtained from the acids of the ether-soluble and ether-insoluble products, point to the presence of lactones in the acids, and it is altogether probable that lactones are also present in the other products given in the table, and that the ether values do not represent alone the amount of glycerin in

¹ "Chemie der Austrocknenden Oele," p. 109.

² *Monatsh. Chem.*, 9, 462 and 463 (1888).

³ *Ibid.*, p. 467.

these unsaponified products, but also the lactones present. Lekowitsch,¹ in an article "On Oxidized Oils," points out the probable presence of lactones in solidified linseed oil (linoleum mass) through the difference in the acid and saponification values from the free acids.

The question has arisen whether or not the product with which we worked, which was insoluble in ether, was identical with Mulder's linoxyn. So far as characteristics are concerned, our ether-insoluble product was identical, except that Mulder says that linoxyn is insoluble in alcohol, while we have found that our product dissolved after long-continued boiling with a large excess of alcohol.² In this, too, our results are at slight variance with Mulder's, so it may be that our product is not identical with Mulder's linoxyn, but it is more than likely that Mulder did not subject his linoxyn to as vigorous a solubility test as we have our product. Reference has already been made to our experiment regarding the solubility of our product (ether-insoluble) in chloroform and alcohol.

The oxidation product which separates from the ligoïn gives a larger amount of ether-soluble product if it is extracted at once than if the product is allowed to stand for some days before extraction. This may be due to a mechanical change in the oxidation product. When first separated, the product is less tenacious and more readily permeated by the solvent, than when it has, by exposure to the air, lost all of the adhering ligoïn by evaporation.

Noerdinger³ has shown that linseed oil varnish will liberate iodine from potassium iodide and has ascribed this liberation to the presence of hydrogen peroxide. We have found that our oxidation product also, when in acetic acid solution, will liberate more iodine than is liberated from a blank test. The question arises whether or not this liberation of iodine from potassium iodide is due to hydrogen peroxide. This we must answer in the negative, for we have been unable to obtain any test for hydrogen peroxide, either with chromic acid or titanous acid. The liberation of the iodine is due to the presence of an organic peroxide.

In conclusion, it should be pointed out that the question of the solubility of the oxidation product (apart from its solubility in glacial acetic acid) was doubtless more or less affected by the presence of the lead and manganese of the drier.

¹ *Analyst*, 27, 139 (1902).

² Except in the case of B₂ as has already been noted.

³ *Pharm. Centrbl.*, 35, 730 (1894).

[FROM THE LABORATORY OF THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION.]

THE PRECIPITATION LIMITS WITH AMMONIUM SULPHATE OF SOME VEGETABLE PROTEINS.

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Received June 27, 1903.

HOFMEISTER and his students, who employed ammonium sulphate with much success in separating different proteins from one another, found that under suitable conditions the individual proteins are precipitated within quite narrow limits when this salt is added to their solutions up to certain degrees of saturation, which to a certain extent are characteristic for each protein. We have, therefore, applied this process to a number of the purer preparations of proteins which we had at our disposal.

A quantity of the protein was dissolved in one-tenth saturated ammonium sulphate solution, the solution filtered clear, and 2 cc. mixed with enough one-tenth saturated sulphate solution to make a final volume of 10 cc. with the saturated sulphate solution to be afterwards added. Successively greater quantities of the saturated solution were used and the points noted at which the solution first became permanently turbid, as well as that at which all the protein was precipitated, as shown by saturating the filtered solution with ammonium sulphate, and observing whether or not a precipitate or turbidity was produced. In many cases the filtrates contained minute quantities of something which was not precipitated with the bulk of the protein under examination, but could be afterwards precipitated from the filtrate by saturating with ammonium sulphate. In these cases we noted the point at which all but this trace was precipitated and also the point at which the solution finally became entirely clear. Whether this trace of substance, which is so much more difficult to precipitate than the bulk of the preparation, was a trace of contaminating proteose or some compound of the protein with some other substance or an alteration product produced by drying or in some other way during preparation, cannot now be told. However, in no case was more than an insignificant trace present and no serious contamination of the preparation is indicated by its presence. The "limits" here given are that at which the solution became turbid immediately after adding the saturated sulphate solution and that at which the protein

was first completely precipitated. Where a considerable further addition of sulphate was necessary to separate the final last trace, the point at which precipitation was practically complete is also given.

To determine the effect of concentration of the protein solution on the results of this determination, we tried the following experiments with neutral edestin.

Concentration of edestin solution. Per cent.	Lower limit. cc.	Upper limit. cc.
9.0	3.0	4.2
4.5	3.1	4.2
2.7	3.0	4.2

When 4.5 per cent. of edestin was dissolved in 10 per cent. sodium chloride, the precipitation limits were lower, namely, 1.8 cc. and 3 cc. Edestin monochloride and edestin sulphate had essentially the same limits as the free edestin, although the lower limit for the sulphate was found to be a little below that of the others.

	Lower limit. cc.	Upper limit. cc.
2.37 per cent. of edestin monochloride.....	3.0	3.9
4.0 " " " " sulphate.....	2.5	4.2

The crystalline globulins of the squash-seed, flaxseed and castor bean are so nearly like that of the hemp-seed that until recently they have been regarded as the same protein. That this similarity extends to their relations toward ammonium sulphate is shown by the following figures:

	Protein. Per cent.	Lower limit. cc.	Upper limit. cc.
Edestin hemp-seed.....	2.7	3.0	4.2
Globulin flaxseed.....	3.4	3.1	4.7
Globulin squash-seed	3.6	3.3	4.4
Globulin castor bean.....	..	3.1	4.5

The globulin of the cottonseed, which we now recognize as another protein than edestin from the hemp-seed, has different precipitation limits from edestin, namely, for a solution containing 2.5 per cent. of globulin, a lower limit of 4.6 cc., and an upper one of 6.4 cc. In this we have another distinction between the cottonseed globulin and edestin. The globulin of the filbert (*Corylus tubulosa*) and that of the English walnut (*Juglans regia*) were

described by Osborne and Campbell¹ under the name of corylin, since a careful comparison of the reactions and analysis of a number of different preparations showed no difference between them. We have recently found² that the globulin of the filbert yields a little more ammonia, when decomposed with hydrochloric acid, than does the globulin of the English walnut, and we must therefore consider them to be distinctly different substances. This conclusion is supported by our determinations of the precipitation limits.

A solution containing 3.4 per cent. of the globulin from the filbert became turbid with 3.7 cc., was almost wholly precipitated with 5.3 cc., and completely with 6.6 cc. Under the same conditions a solution containing 2.75 per cent. of globulin from the English walnut became turbid with 2.8 cc., was almost wholly precipitated by 4.6 cc. and completely precipitated with 6.6 cc. That the last traces were precipitated, after nearly all of the globulin had been thrown out of solution, only by adding a considerably greater quantity of sulphate, indicates a slight contamination of the preparation with some other protein, possibly a trace of adhering proteose, possibly an alteration product of the globulin formed during drying or otherwise. However this may be, the amount was too small to be of serious consequence. The globulin of the American black walnut showed exactly the same behavior toward ammonium sulphate as that of the English walnut.

It is hence evident that the globulin of the English walnut is a different substance from that of the filbert and the name corylin should therefore be applied only to the latter.

Excelsin from the brazil nut and amandin from the almond have nearly the same precipitation limits although, otherwise, they are distinctly different substances. The lower limit for excelsin was found to be 3.8 cc., the upper 5.5 cc., while for amandin the lower limit was 3.5 cc. and the upper limit 5.3 cc. Preparations of legumin from different seeds, which have as yet appeared to be in all respects alike, showed the same precipitation limits with ammonium sulphate.

	Lower limit. cc.	Upper limit. cc.
1.8 per cent. legumin, vetch.....	5.2	7.3
3.2 per cent. legumin, horse bean.....	5.4	7.5
2.6 per cent. legumin, lentil.....	5.5	7.4

¹ This Journal, 18, 609 (1896); also Report of the Conn. Agr. Expt. Station for 1895, p. 268.

² This Journal, 25, 423 (1903).

Nearly all the legumin was precipitated in each case by 6.5 cc., that remaining in solution with more than this quantity being very little.

The globulin of the castor bean is partly precipitated from its concentrated solutions in 10 per cent. sodium chloride by saturating its solution with this salt. The precipitate thus produced, when redissolved in dilute brine, is again partly thrown out by saturating with sodium chloride, and as often as this process is repeated a considerable part of the globulin remains dissolved in the saturated salt solution. From this it seems more probable that the globulin has a limited solubility in saturated sodium chloride solution, which is much less than that in a 10 per cent. brine, than that two different globulins exist in the seed. The precipitation limits with ammonium sulphate also indicate that this is the case, as the following experiment shows. A quantity of this globulin, obtained by dialyzing a sodium chloride extract of castor beans, was dissolved in a moderate quantity of 10 per cent. brine, and the solution saturated with sodium chloride. The large precipitate was filtered out, again dissolved in brine, and the solution saturated with sodium chloride. The second precipitate appeared to be less than the first. The solution and precipitate were again repeated, when the final precipitate was dissolved in brine, and this solution, as well as the three filtrates from the precipitates produced by saturation, were dialyzed till free from sodium chloride. The substance separated from all four solutions as a mixture of crystals and spheroids, which were washed with water and dehydrated with absolute alcohol. After drying over sulphuric acid, the different preparations weighed as follows:

No. 1. 8.67 grams. This was the final precipitate produced by saturating with sodium chloride.

No. 2. 6.2 grams. The globulin remaining in solution after precipitating No. 1.

No. 3. 13 grams. The globulin remaining in solution after the second precipitation.

No. 4. 12.8 grams. The globulin remaining in solution after the first precipitation.

Since the substance yielding 1, 2 and 3 was precipitated by the first saturation with sodium chloride and two-thirds of this remained in solution after saturating the second and third time, it is

evident that precipitation is simply due to a limited solubility of this globulin in saturated salt solution. The smaller weight of No. 2 is due to the smaller volume of the solution from which it was obtained.

The precipitation limits of these preparations were as follows :

	Lower limit. cc.	Upper limit. cc.
No. 1.....	3.1	4.4
No. 3.....	3.16	4.5
No. 4.....	3.4	4.8

The slightly higher limits shown by No. 4 differ too little from those of the others to warrant the conclusion that two different proteins exist in these preparations.

The seeds of the yellow lupine contain a large amount of protein matter which can be separated into two extremes by fractional precipitation, which differ slightly from one another in properties and composition, especially in sulphur content, the more soluble fraction containing three times as much sulphur as the less soluble.

The precipitation limits were as follows :

	Lower limit. cc.	Most precipitated between.		Upper limit. cc.
		cc.	cc.	
Conglutin (a) less soluble	4.2	4.3	6.0	7.3
Conglutin (b) more soluble	4.6	6.4	8.2	8.7

From these results it is evident that the two extremes represent different proteins and that the more soluble one is precipitated at a much higher saturation than the less soluble one. It also appears that the separation of these two proteins from one another in the case of the preparations here tested, was not entirely complete.

The globulin from the blue lupine showed nearly the same behavior as the less soluble globulin of the yellow lupine, the lower limit being 4.4 cc., while with 6 cc. nearly all was precipitated.

Phaseolin is more soluble in strong solutions of ammonium sulphate than any protein we have yet examined. The lower limit was found with 6.4 cc. With 8.2 cc., which was all that could be added, under the conditions of the test as applied to the other globulins, there was still considerable protein in solution. When 1 cc. of the phaseolin solution was mixed with 9 cc. of the saturated solution all was precipitated. The upper limit appears to be, therefore, a little below 9 cc. The following table contains the

results of these determinations, arranged in the order of the solubility of each protein substance in ammonium sulphate solution.

Protein.	Lower limit.	Most precipitated.		Upper limit.
	cc.	cc.	cc.	cc.
Globulin, English walnut	2.8	2.8	4.6	6.6
Globulin, black walnut.....	2.8	2.8	4.6	6.6
Edestin	3.0	3.0	4.0	4.2
Edestin monochloride	3.0	3.0	3.9	3.9
Globulin flaxseed.....	3.1	3.3	4.6	4.7
Globulin castor bean	3.1	3.3	4.3	4.5
Globulin squash-seed.....	3.3	3.5	4.1	4.4
Amandin.....	3.5	3.5	5.0	5.3
Corylin	3.7	3.7	5.3	6.6
Excelsin.....	3.8	4.0	5.0	5.5
Conglutin (a).....	4.2	4.3	6.0	7.3
Conglutin (b).....	4.6	6.4	8.2	8.7
Globulin cottonseed	4.6	5.0	6.0	6.4
Legumin	5.4	5.5	6.5	7.5
Phaseolin.....	6.4	6.5	8.2	8.8

[FROM THE LABORATORY OF THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION.]

THE SPECIFIC ROTATION OF SOME VEGETABLE PROTEINS.

By THOMAS B. OSBORNE AND ISAAC F. HARRIS.

Received June 27, 1903.

THE specific rotation of very few of the vegetable proteins has been determined, the only observations, so far as we know, being those of Kjeldahl¹ on zein and gliadin, Alexander² on edestin, excelsin and the globulin of the flaxseed, and Chittenden and Mendel³ on edestin. Having had an opportunity to make some observations on the proteins above named, as well as on a few others, we take this occasion to put them on record.

The determinations were made with a Schmidt and Haensch half-shade polariscope, provided with a sugar scale. The readings were calculated to degrees of circular polarization by multiplying the degrees observed on the sugar scale by 0.346. The results

¹ Kjeldahl: *Agricultur. Chem. Centrbl.*, 25, 197 (1896).

² Alexander: *Jour. Expt. Med.*, 1, No. 2 (1896).

³ Chittenden and Mendel: *Jour. Physiol.*, 17, 40 (1894).

given were in all cases the average of a large number of observations, which in most cases agreed closely. The solutions of some of the proteins, although uncommonly clear and very nearly free from opalescence, were so opaque in long layers that satisfactory readings could be made only in comparatively dilute solutions and therefore the accuracy of these determinations was to a greater or less extent impaired.

The amount of dissolved protein was found by determining nitrogen in the contents of the polariscope tube, the capacity of which was accurately known. The amount of protein was obtained by multiplying the quantity of nitrogen found by a factor depending on the nitrogen content of the protein examined.

EDESTIN.

The preparation used had been repeatedly recrystallized and was perfectly neutral to phenolphthalein. A solution in 10 per cent. sodium chloride brine was filtered clear through a felt of paper pulp and examined with the following results:

- I. α = observed rotation -2.7° .
 w = weight of protein per cubic centimeter 0.03385 gr.
 l = length of tube 2 dm.
 $(\alpha)_D^{20} = -40^\circ$.
- II. $\alpha = -2.07^\circ$ $w = 0.0247$ gram $l = 2$ dm.
 $(\alpha)_D^{20} = -41.9^\circ$.
- III. $\alpha = -5.05^\circ$ $w = 0.06095$ gram $l = 2$ dm.
 $(\alpha)_D^{20} = -41.43^\circ$.
- IV. $\alpha = -2.53^\circ$ $w = 0.0610$ gram $l = 1$ dm.
 $(\alpha)_D^{20} = -41.47^\circ$.

Another pure preparation of edestin gave the following results:

- V. $\alpha = -1.73^\circ$ $w = 0.0415$ gram $l = 1$ dm.
 $(\alpha)_D^{20} = -41.7^\circ$.

The average of these results, -41.3° , agrees closely with that obtained by Alexander, namely, -41.6° , and does not differ greatly from that given by Chittenden and Mendel, -43° . There is no evidence that the degree of rotation is dependent on the concentration of the solution.

EXCELSIN.

The preparation of excelsin which we used was extracted from the brazil nut by sodium chloride brine and purified by recrystal-

lization. Although the solution in 10 per cent. sodium chloride brine used for polariscopic examination was almost free from every trace of opalescence, nevertheless, it was difficult to get satisfactory readings in strong solutions. Our results were as follows:

- I. $\alpha = -3.38^\circ$ $w = 0.0396$ gram $l = 2$ dm.
 $(\alpha)_D^{20} = -42.68^\circ$.
- II. $\alpha = -3.95^\circ$ $w = 0.0463$ gram $l = 2$ dm.
 $(\alpha)_D^{20} = -42.66^\circ$.
- III. $\alpha = -2.00^\circ$ $w = 0.0460$ gram $l = 1$ dm.
 -43.48° .

The average of our figures, -42.94° , is considerably higher than that of Alexander, -40.3° , but, as he appears to have been unable to get such clear solutions as we did and had great difficulty in making his readings, it is probable that our results are the more correct.

FLAXSEED GLOBULIN.

The carefully purified preparation of this globulin consisted of well-formed octahedral crystals, the solution of which, in 10 per cent. sodium chloride brine, when filtered, was so transparent that accurate readings were easily made.

- I. $\alpha = -3.63^\circ$ $w = 0.0415$ gram $l = 2$ dm.
 $(\alpha)_D^{20} = -43.73^\circ$.
- II. $\alpha = -1.79^\circ$ $w = 0.0413$ gram $l = 1$ dm.
 $(\alpha)_D^{20} = -43.34^\circ$.

The average of these determinations, -43.53° , is much higher than that found by Alexander, who gives -38.7° as the mean of six observations on different solutions. This difference may be due to the much greater concentration of our solutions, as Alexander's results strongly indicate a considerable decrease in the specific rotation with decreasing percentage content of the solution in protein.

SQUASH-SEED GLOBULIN.

The squash-seed globulin was purified by repeatedly recrystallizing and found to have the following rotation when dissolved in 10 per cent. sodium chloride solution:

- I. $\alpha = -4.70^\circ$ $w = 0.0598$ gram $l = 2$ dm.
 $(\alpha)_D^{20} = -39.3^\circ$.
- II. $\alpha = -4.12^\circ$ $w = 0.0534$ gram $l = 2$ dm.
 $(\alpha)_D^{20} = -38.57^\circ$.
- III. $\alpha = -2.05^\circ$ $w = 0.0535$ gram $l = 1$ dm.
 $(\alpha)_D^{20} = -38.32^\circ$.

If we compare the average of these figures with those of the flaxseed globulin and of edestin, which were obtained with solutions of approximately the same strength, we find them as follows:

	$(\alpha)_D^{20}$.
Edestin.....	41.30°
Flaxseed globulin.....	43.34°
Squash-seed globulin.....	38.73°

These three globulins appear therefore to differ in rotatory power to such a degree that the differences cannot be attributed to experimental errors. Although alike in composition, reactions, solubility and crystalline form, we have recently shown¹ that these globulins yield such different proportions of the several classes of nitrogenous decomposition products that there can be no question but that they are different substances. To these differences must now be added those in specific rotatory power.

AMANDIN.

Amandin, the chief protein constituent of almonds and peach-seeds, when dissolved in 10 per cent. sodium chloride solution, was found to have the following specific rotation:

$$\alpha = -2.98^\circ \quad w = 0.0264 \text{ gram} \quad l = 2 \text{ dm.}$$

$$(\alpha)_D^{20} = -56.44^\circ.$$

CORYLIN.

Corylin is a globulin which is abundantly present in the hazel nut or filbert. Dissolved in 10 per cent. sodium chloride solution it showed the following rotatory power:

- I. $\alpha = -2.87^\circ$ $w = 0.0332$ gram $l = 2$ dm.
 $(\alpha)_D^{20} = -43.22^\circ$.
- II. $\alpha = -1.40^\circ$ $w = 0.0326$ gram $l = 1$ dm.
 $(\alpha)_D^{20} = -42.95^\circ$.

¹ Osborne and Harris: This Journal, 28, 323 (1903).

THE GLOBULIN OF THE ENGLISH WALNUT.

The English walnut contains a globulin which so closely resembles corylin in its properties and composition that the writer¹ was led to regard it as probably identical with that substance. We have since found that it yields, on decomposition, a slightly, but distinctly, smaller amount of ammonia than does corylin and that a difference between the two is shown by the precipitation limits with ammonium sulphate. In harmony with this, we find a slight difference in the specific rotation of their solutions in 10 per cent. sodium chloride brine, as the following figures show:

- I. $\alpha = -1.57^{\circ}$ $w = 0.0357$ gram $l = 1$ dm.
 $(\alpha)_{D}^{20} = -44^{\circ}$.
- II. $\alpha = -2.06^{\circ}$ $w = 0.0227$ gram $l = 2$ dm.
 $(\alpha)_{D}^{20} = -45.37^{\circ}$.
- III. $\alpha = -1.05^{\circ}$ $w = 0.0227$ gram $l = 1$ dm.
 $(\alpha)_{D}^{20} = -46.25^{\circ}$.

The considerable differences between the above observations are chiefly due to the opacity of the solutions which, though filtered very clear, were, in a remarkable degree, impervious to light.

The specific rotation of the globulin of the English walnut is distinctly higher than that of the filbert, thereby showing another difference between these two very similar proteins.

THE GLOBULIN OF THE AMERICAN BLACK WALNUT.

The American black walnut is closely related to the English walnut and we have therefore made a close comparison of the globulins from these two nuts, but have discerned no notable difference between them. As the following figures show, the specific rotation of the globulin from American nut is practically the same as that of the one from English, the difference between the figures given being doubtless due to errors of observation caused by the opacity of the solutions. Dissolved in 10 per cent. sodium chloride solution, the following results were obtained:

- I. $\alpha = -1.22^{\circ}$ $w = 0.0272$ gram $l = 1$ dm.
 $(\alpha)_{D}^{20} = -44.85^{\circ}$.
- II. $\alpha = -1.20^{\circ}$ $w = 0.0273$ gram $l = 1$ dm.
 $(\alpha)_{D}^{20} = -44.0^{\circ}$.

¹ Osborne and Campbell: *This Journal*, 18, 609.

PHASEOLIN.

Phaseolin, which constitutes the greater part of the protein matter of the kidney bean (*Phaseolus vulgaris*), was found to have the following rotation when a crystallized preparation was dissolved in 10 per cent. sodium chloride solution:

- I. $\alpha = -7.42^\circ$ $w = 0.0900$ gram $l = 2$ dm.
 $(\alpha)_D^{20} = -41.22^\circ$.
- II. $\alpha = -3.75$ $w = 0.0900$ gram $l = 1$ dm.
 $(\alpha)_D^{20} = -41.7^\circ$.

LEGUMIN.

A solution of a very pure preparation of legumin from the horse bean (*vicia faba*) was made with 10 per cent. of sodium chloride and found to have the following specific rotation:

- I. $\alpha = -2.2^\circ$ $w = 0.0494$ gram $l = 1$ dm.
 $(\alpha)_D^{20} = -44.53^\circ$.
- II. $\alpha = -1.27^\circ$ $w = 0.0291$ gram $l = 1$ dm.
 $(\alpha)_D^{20} = -43.64^\circ$.

ZEIN.

The principal protein of maize kernels is zein, which is soluble in strong alcohol. A solution of zein in alcohol of 90 per cent. by volume rotated as follows:

- I. $\alpha = -3.03^\circ$ $w = 0.0536$ gram $l = 2$ dm.
 $(\alpha)_D^{20} = -28.26^\circ$.
- II. $\alpha = -1.45^\circ$ $w = 0.0523$ gram $l = 1$ dm.
 $(\alpha)_D^{20} = -27.72^\circ$.

GLIADIN.

Gliadin, which forms about one-half of the protein of wheat gluten, when dissolved in alcohol, of 80 per cent. by volume, showed the following specific rotation:

- I. $\alpha = -5.66^\circ$ $w = 0.0308$ gram $l = 2$ dm.
 $(\alpha)_D^{20} = -91.9^\circ$.
- II. $\alpha = -2.86^\circ$ $w = 0.0309$ gram $l = 1$ dm.
 $(\alpha)_D^{20} = -92.55^\circ$.

The following table contains the specific rotation as determined for each of the preceding proteins:

Protein.	Source.	$(\alpha)_D^{20}$.
Edestin	Hemp-seed	-41.3°
Globulin	Flaxseed	-43.53°
Globulin	Squash-seed	-38.73°
Excelsin	Brazil nut	-42.94°
Amandin	Almonds	-56.44°
Corylin	Filbert	-43.09°
Globulin	English walnut	-45.21°
Globulin	Black walnut	-44.43°
Phaseolin	Kidney bean	-41.46°
Legumin	Horse bean	-44.09°
Zein	Maize	-28.00°
Gliadin	Wheat	-92.28°

[FROM THE LABORATORY OF THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION.]

THE GLOBULIN OF THE ENGLISH WALNUT, THE AMERICAN BLACK WALNUT AND THE BUTTERNUT.

BY THOMAS B. OSBORNE AND ISAAC F. HARRIS.

Received June 27, 1903.

PROTEINS, whose chemical identity is probable, have thus far been found only in seeds which are botanically closely related to each other.

Thus the chemical identity of gliadin from wheat or rye, of legumin from vetches, horse beans, lentils or peas, of vicilin from the three latter seeds, of phaseolin from the kidney or adzuki beans and of legumelin from the seeds of numerous legumes appears to be highly probable.

The strict chemical identity of carbon compounds of such high molecular weight can, of course, not be positively asserted, since the possibility of isomeric or homologous compounds of very similar properties is great. However, a rigid comparison of these supposedly identical proteins has as yet shown no difference whatever between them. Some proteins, which we had formerly regarded as identical, have recently been found to differ in the proportions of their various decomposition products, and it is certain that their molecules have a different structure. All these proteins were found in seeds which were *not* botanically closely related and should therefore, by analogy, *not* contain the same proteins. So marked is this difference in the protein constituents

of the different seeds that the question may be asked: Is not this chemical difference in the food of the growing embryo an important factor in determining the nature of the developing organism?

Now that wide differences in the structure of the molecules of the different proteins are more fully recognized, it seems probable that the course of the chemical reactions, leading to the development of the growing embryo, will be largely influenced by the nature of the protein food presented to it at the beginning of its existence. Whether similar differences in the protein food of the animal embryo exists is not so definitely determined, but the few facts on record point strongly that way, for Panormoff's investigations indicate that hen's, dove's and crow's eggs contain distinctly different albumins.

The closest resemblance between proteins from unrelated seeds which we have as yet encountered is presented by corylin from the filbert (*corylus*) and the globulin from the English walnut (*Juglans regia*), the only difference, as yet discovered, being a slightly smaller yield of ammonia by the latter, when decomposed with hydrochloric acid, and a slight difference in the precipitation limits with ammonium sulphate.

In order to see if the same relations would be shown by the globulins from the botanically, closely related American black walnuts and butternuts (*Juglans nigra* and *J. cinera*) we have examined these nuts with the following results.

THE GLOBULIN OF THE BLACK WALNUT (*Juglans nigra*).

The nuts were freed from their shells, crushed, the greater part of the oil pressed out and the remainder extracted with ether. The residual meal was then extracted with 10 per cent. sodium chloride solution, the extract filtered clear and dialyzed. The globulin was deposited in spheroids which were filtered out, washed thoroughly with water and then with alcohol, and dried over sulphuric acid. Dried at 110°, this preparation had the following composition:

BLACK WALNUT GLOBULIN, PREPARATION I.

Carbon	50.95
Hydrogen	7.10
Nitrogen	18.84
Sulphur	0.78
Oxygen	22.33
	<hr/>
	100.00
Ash	0.38

This preparation was then dissolved in 10 per cent. sodium chloride solution, a large quantity of the insoluble form of the globulin filtered out and the clear solution dialyzed for several days. The globulin, which again precipitated in spheroids, was filtered out, washed with water and with alcohol and dried over sulphuric acid. The 32 grams thus secured, which formed about one-half of the original material, had, as the following figures show, essentially the same composition, when dried at 110°, as the preparation from which it was derived.

BLACK WALNUT GLOBULIN, PREPARATION 2.

	I.	II.
Carbon	51.06	51.07
Hydrogen.....	6.87	6.84
Nitrogen	18.96	18.96
Sulphur.....	0.77
Oxygen.....	22.34
	<hr/> 100.00	
Ash.....	0.33	

This preparation was almost wholly soluble in 10 per cent. sodium chloride solution and showed the same reactions as those given in an earlier paper for the globulin of the English walnut.¹ A solution containing about 5 per cent. of the globulin and 10 per cent. of the sodium chloride remained clear until heated to 99°, when it became turbid and, after continued heating, yielded a considerable coagulum. Solutions of the globulin from the English walnut yielded a trace of coagulum at lower temperatures, which was unquestionably due to a trace of another protein, adhering to the preparation in minute quantity. Saturation of the solution with sodium chloride gave a very slight precipitate and with magnesium sulphate a very considerable one, in this respect exactly resembling the globulin of the English walnut. The other reactions were also, in all respects, the same.

When decomposed by boiling with strong hydrochloric acid, the proportion of nitrogen in the different forms of binding were as follows:

N as NH ₃ .	Basic N.	Non-basic N.	N in MgO precipitate.	Total.
1.71	5.61	11.45	0.19	18.96
1.86	5.85	10.92	0.33
1.83	5.85	11.04	0.24

The specific rotation of this globulin was determined as follows:

¹ This Journal, 18, 609 (1896).

Solvent.	Amount per cc. Gram.	Observed rotation.	Length of tube.	Specific rotation. (α) _D ²⁰ =
10 % NaCl	0.0272	1.22°	1 dm.	-44.85°
.....	0.0273	1.20°	1 dm.	-44.0°

The precipitation limits with ammonium sulphate were determined by making a 2.7 per cent. solution of the globulin in one-tenth saturated ammonium sulphate solution and then adding different quantities of a saturated solution of ammonium sulphate to 2 cc. of the globulin solution previously diluted with enough one-tenth saturated to make a final volume of 10 cc.

The mixture became turbid when the amount of sulphate was equal to that in 2.8 cc. of a saturated solution. When sulphate equal to 4.6 cc. was added, only a very minute quantity of protein remained unprecipitated, which was doubtless a trace of some other adherent protein. With less than 4.6 cc. the amount in solution was greater. The precipitation limits are therefore 2.8 cc. and 4.6 cc.

THE GLOBULIN OF BUTTER NUT (*Juglans cinerea*).

The preparation of this globulin, which we examined, was very kindly given to us by Dr. A. L. Dean, of Yale University, for which we here wish to express our thanks. Dr. Dean extracted the crushed meats of the nut with petroleum ether and exhausted the residual meal with 10 per cent. sodium chloride solution. The clear, filtered extract was dialyzed in running water for seven days when the globulin, which separated in spheroids, was filtered out and washed with water, with alcohol and with ether. As the quantity of the globulin was not sufficient for further purification by reprecipitation, it was examined in the condition in which it was received.

Dried at 110° it had the following composition:

BUTTER-NUT GLOBULIN, PREPARATION I.

Carbon	50.85	50.91
Hydrogen.....	6.79	6.88
Nitrogen.....	18.62	18.59
Sulphur	0.80
Oxygen	22.94
	<hr/> 100.00	
Ash.....	3.54	3.67

This preparation was almost completely soluble in 10 per cent. sodium chloride solution and showed throughout the same reactions as those given by the globulins of the English and black walnut.

When decomposed by boiling with strong hydrochloric acid, the proportion of nitrogen in the different groups of nitrogenous decomposition products was as follows:

N as NH_3 .	Basic N.	Non-basic N.	N in MgO precipitate.	Total.
1.83	5.77	10.87	0.14	18.61

The specific rotation of this globulin was found as follows:

Solvent.	Amount per cc.	Observed rotation.	Length of tube.	Specific rotation. $(\alpha)_D^{20} =$
10 % NaCl	0.0212	1.97°	2 dm.	-46.9°
10 % NaCl	0.0223	0.98°	1 dm.	-43.9°

The precipitation limits of a 4 per cent. solution of the globulin, dissolved in one-tenth saturated ammonium sulphate, were determined in the same manner as for the black walnut globulin and found to be 3.1 cc. and 5.5 cc., the amount remaining in solution with 5.5 cc. being more than in the case of the black walnut, at the higher limit, which was doubtless due to the lack of sufficient purification of this preparation, and possibly also to a difference in acidity between the preparations examined.

SUMMARY.

In the following table the results of our examination of the globulin from the seeds of the three species of *Juglans* are brought together for comparison with those of the globulin of the filbert, *Corylus*.

COMPOSITION.

	<i>J. regia</i> .	<i>J. nigra</i> .	<i>J. cinerea</i> .	<i>Corylus</i> .
Carbon	50.80	51.07	50.88	50.72
Hydrogen	6.84	6.86	6.84	6.86
Nitrogen	18.96	18.96	18.62	19.02
Sulphur	0.80	0.77	0.80	0.83
Oxygen	22.51	22.33	22.86	22.57
	100.00	100.00	100.00	100.00

PERCENTAGE OF NITROGEN IN THE GROUPS OF NITROGENOUS DECOMPOSITION PRODUCTS.

	N as NH_3 .	Basic N.	Non-basic N.	N in MgO precipitate.
<i>J. regia</i>	1.84	6.08	10.93	0.11
<i>J. nigra</i>	1.80	5.77	11.14	0.25
<i>J. cinerea</i>	1.83	5.77	10.87	0.14
<i>Corylus</i>	2.20	5.75	10.70	0.16

SPECIFIC ROTATION $(\alpha)_D^{20}$.

<i>J. regia</i>	-45.21°
<i>J. nigra</i>	-44.42°
<i>J. cinerea</i>	-45.40°
<i>Corylus</i>	-43.09°

PRECIPITATION LIMITS WITH AMMONIUM SULPHATE.

<i>J. regia</i>	2.8 cc.	-4.6 cc.
<i>J. nigra</i>	2.8 cc.	-4.6 cc.
<i>J. cinerea</i>	3.1 cc.	-5.5 cc.
<i>Corylus</i>	3.7 cc.	-5.3 cc.

The only positive difference shown by the preparations from these four seeds is the greater quantity of N yielded as ammonia by the globulin from the filbert (*Corylus*). This difference exceeds the limits of experimental error by too great an amount to be overlooked and may be taken as evidence that the globulin of *Corylus* differs in structure from that of *Juglans*. A positive difference between the corylin and the globulin from *J. regia* and *J. nigra* is also shown by the precipitation limits with ammonium sulphate. This difference, however, is not very great and, in view of our ignorance of the extent to which these limits may be altered by slight differences in the conditions of experimentation, cannot be considered as conclusive evidence, though it strongly indicates a difference between the globulins.

The precipitation limits of the globulin from *J. cinerea* are higher than those found for *J. regia* and *J. nigra*, but in view of the very close agreement between these preparations in all other respects we are inclined to attribute this difference to the greater purity of the preparations from the latter seeds.

In consequence of these facts, it seems desirable to give a name to the globulin of *Juglans*, retaining the designation corylin for the globulin of *corylus*. We propose therefore to call the principal protein which we have obtained from the nuts of the three species of the former genus Juglansin.

The botanical relations which are shown by the proteins of seeds deserve further careful study, as it is not improbable that the natural relations of some plants may be thus discovered.

[FROM THE LABORATORY OF THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION.]

THE TRYPTOPHANE REACTION OF VARIOUS PROTEINS.

BY THOMAS B. OSBORNE AND ISAAC F. HARRIS.

Received June 27, 1903.

As LONG ago as 1831, Tiedemann and Gmelin recognized among the decomposition products of protein bodies a substance whose solution was colored a deep violet-red with chlorine or bromine. The nature of this substance remained wholly unknown until Hopkins and Cole recently succeeded in isolating it in a state of purity and recognizing it as most probably indol-amino-propionic

acid or the isomeric skatol-amino-acetic acid. They also found that this substance yielded the violet reaction with acetic and sulphuric acid, which has long been known as Adamkiewicz's reaction. This latter reaction they further found was caused by glyoxylic acid contained in the acetic acid, and they have therefore substituted glyoxylic acid for acetic acid in applying this test. This observation is of much importance, as formerly the Adamkiewicz reaction was attributed to furfural and the presence of carbohydrates was therefore inferred among the protein decomposition products.

In the following table we give the results of the application of the Hopkins-Cole reagent to a number of different proteins, 50 mg. of each being mixed with 6 cc. of the glyoxylic acid solution and 6 cc. of concentrated sulphuric acid added.

Zein, maize ; very pale straw color ; no reaction.	
Alcohol-soluble protein, oat kernel ; light brownish ; no violet tint.	
Bynin, malt ; red-brown ; no violet tint whatever.	
Vicilin, pea ; very pale violet ; hardly any reaction.	
Phaseolin, kidney bean ; pale violet ; a little stronger than vicilin.	
Avenalin, oat kernel ; light violet color.	
Globulin, wheat ; light violet color.	
Hordein, barley ;	
Legumin, vetch ;	
Legumin, lentil ;	
Legumin, horse bean ;	
Vignin, cow pea ;	
Conglutin, yellow lupine ;	
Conglutin, blue lupine ;	
Amandin, almond ;	
Glycinin, soy bean ;	
Gliadin, wheat ;	
Ovovitellin, hen's egg ;	
Globulin, sunflower ;	
Glutenin, wheat ;	
Globulin, castor bean ;	
Edestin, hemp ;	
Excelsin, Brazil nut ;	
Corylin, filbert ;	
Conalbumin, egg white ;	
Ovalbumin, egg white ;	
Globulin, flaxseed ;	
Globulin, squash-seed ;	
Globulin, black walnut ;	
Globulin, English walnut ;	
Leucosin, wheat ;	

The intensity of the reaction increased gradually from hordein to leucosin, the former giving a positive reaction, the latter a strong one.

Whether any of the above proteins wholly lack the tryptophane group could not be determined, as we were able to get a very slight reaction with a relatively large quantity of zein by cautiously adding the sulphuric acid up to one-half the volume of the glyoxylic acid. The color thus produced was, at the most, very slight and transitory. With the alcohol-soluble proteins of the oat and barley malt, the brown color was sufficient to obscure a slight violet reaction, and the result of the test in these cases was not conclusive.

It is interesting to note the very marked difference in the intensity of the reaction with the proteins at the two ends of the table and it is fair to presume that the proportion of tryptophane yielded by the several proteins differs considerably.

[CONTRIBUTIONS FROM THE BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE, No. 49.]

DISAPPEARANCE OF REDUCING SUGAR IN SUGAR-CANE.

By H. W. WILEY.

Received June 11, 1903.

THE occurrence of reducing sugar in sugar canes and sorghums has important relations to the metabolism of the plants. Presumably the carbohydrate which is finally formed in the chlorophyll cells of these plants is some variety of starch, probably a soluble variety, since starch granules, as such, would find obstructions to circulation in the return currents from the leaves to the body of the plant. During the early stages of growth it has been shown by repeated analyses that the proportion of reducing sugar to sucrose in the juices of the sugar cane is very high. In Louisiana, where the canes are harvested necessarily before growth is complete, the average quantity of reducing sugars in the juice is 1 per cent. or more. In the tropics at the time of harvest the percentage of reducing sugars is very much less, usually less than 0.5 per cent. These facts show beyond doubt that the highest relative value of reducing sugar to sucrose is in the earlier stages of growth and the lowest proportion in the matured stages. Theoretically, then, we might expect that at a certain period representing the complete and perfect maturity of the plant the reducing sugar would disappear. The further

phenomenon, however, has also been observed, namely, that when the reducing sugar has been reduced to a minimum on approaching maturity, any deterioration in the plant, due to long standing, overripeness, injury (from frosts or otherwise), tends to reverse the order observed during the growing period, and to increase the percentage of the reducing sugar at the expense of the sucrose. This reversibility of enzymic action has been well established in the case of carbohydrates.¹ If the sugar cane, therefore, be allowed to normally grow and mature, there is a certain time in its history, as above mentioned, where the proportion of reducing sugar is at a minimum. The theory above outlined receives confirmation in some analytical data secured in this bureau recently on samples of sugar cane grown in Florida. Four samples were obtained which were all harvested at the same time, namely, the middle of May, 1903. The canes were grown by W. H. Abel, on Terra Ceia Island, Manatee County, Florida, about 150 yards from salt water. The soil is sandy to a depth of from 12 to 18 inches, with a thin stratum of chocolate-colored subsoil resting on clay, which carries some pebble phosphate. The particular samples under question were grown on the edge of a field next to timber, and being in the outside row, did not get much cultivation and practically no fertilizer. The samples were cut seventeen months from time of planting. The analytical data obtained from the four samples are as follows:

COMPOSITION OF THE JUICE.

Density. Per cent.	Sucrose. Per cent.	Purity.	Glucose.
21.0	19.0	90.5	None
20.8	18.7	90.0	None
20.4	18.0	88.2	None
21.7	19.8	91.2	None

These are the only samples of sugar cane ever analyzed under my supervision which did not contain a greater or less quantity of reducing sugar. At the end of two minutes' boiling of the juices with an alkaline copper solution, there was no trace whatever of any reduction. On longer continued boiling and after allowing to stand over night, there was a mere trace of reddish precipitate, due doubtless to the inversion of a part of the sucrose. A great many of the canes grown on this field produced tassels, but Mr. Abel did not state in his description whether the four canes sent had

¹*Jour. Chem. Soc. Trans.*, May, 1903, p. 578.

tasseled or not. The presumption is that they had. We have in the above what appears to be an example of a complete cycle of growth in the sugar cane, probably a cycle which would not be realized farther south. Evidently the cool nights of the winter had helped to complete the period of growth, while at the same time they prevented a beginning of the second growth, which would certainly have reversed the metabolic activities within the cane and secured an inversion of a part of the sucrose. It is probable that the meteorological conditions which produced so complete a growth do not often obtain and the above data are therefore of interest, both from a chemical and physiological point of view. The analyses were made in the Sugar Laboratory by Mr. Arthur Given.

COLORING-MATTER IN YELLOWISH GRAY SUGAR.

BY Y. NIKAIIDO.

Received June 27, 1903.

THE crystallized sugar we obtained from the last few straight pans in the 1902 campaign, at the sugar factory operated by the Standard Beet Sugar Co., Leavitt, Neb., acquired a slight yellowish gray tint. The samples were saved and subjected to investigation. Since we could not make a series of investigations at this time of the year, the work is not complete, but some of the statements may be interesting to sugar-makers.

Herzfeld considers iron oxide as one of the causes of the gray coloration of crystallized sugar.¹ For this reason, the sample of sugar in question was tested qualitatively. Iron oxide, lime, soda and potash salts and a little organic coloring-matter were found in it. In order to ascertain how much iron oxide in the massecuite is sufficient to produce a yellowish tint in the sugar crystals, the quantity of the iron oxide in the massecuite sample was estimated and found to be 0.02 per cent. As it seemed doubtful that such a small amount of iron oxide in the massecuite would cause the coloration of sugar crystals, complete analyses of the massecuite and ash of the same were made and the results obtained were as follows:

¹ *Ztschr. Rubenzuckerind.*, 46, 1 (1896).

MASSECUITE.

Constituents.	Per cent. in water-free material.
Sucrose.....	84.76
Invert sugar	0.93
Raffinose	2.38
Ash	3.34
Organic matter.....	8.57
Iron oxide	0.02
	<hr/>
	100.00

COEFFICIENTS CALCULATED.

	Per cent.
Total solid.....	89.83
Water	10.17
Polariscope reading	79.90
True purity	84.76
Saline coefficient	25.38
Glucose coefficient	1.10
Coefficient of organic matter	9.89

ASH.

	Per cent.
Acid-insoluble matter (mostly silica)	0.80
Iron oxide (Fe_2O_3)	0.65
Calcium carbonate	13.86
Sodium chloride	7.06
Sodium carbonate.....	16.99
Potassium sulphate.....	28.94
Potassium carbonate.....	29.80
Magnesia	trace
Moisture and undetermined	1.90
	<hr/>
	100.00

According to these analyses, excepting raffinose, there is no unusual constituent in this massecuite, judging from the analysis of another massecuite which yielded a good quality of white sugar. For the purpose of comparison, a statement of this analysis is here given:

Composition.	Per cent. in water-free material.
Sucrose.....	83.83
Invert sugar	3.34
Raffinose	none
Ash	4.88
Organic matter.....	7.95
Iron oxide, less than	0.01
	<hr/>
	100.00

COEFFICIENTS CALCULATED.

	Per cent.
Total solid.....	90.50
Water	9.50
Polariscope reading	79.00
True purity	83.83
Saline coefficient.....	17.17
Glucose coefficient	3.98
Coefficient of organic matter	9.48

Raffinose in considerable quantity is said to have the effect of changing the normal form of sugar crystals, producing needles, but it has nothing to do with the coloring of the sugar. It may, therefore, safely be said that the coloring of our sugar was principally due to the iron oxide, although the other impurities might have played some part. It would be worth noting that even such a small quantity of iron oxide as 0.02 per cent. is sufficient to cause coloration of sugar crystals.

In order to trace the source of the iron oxide, the limestone used for defecation was analyzed. It seemed possible that the rock might have contained an unusually large quantity of iron oxide. Since *oxide of iron is soluble in sugar solution even in the presence of alkali*, it was reasonable to suppose that iron might have been thus introduced in the carbonation process. The results of the limestone analysis are as follows:

	Per cent.
Moisture.....	trace
Insoluble matter	1.96
Organic matter	trace
Alumina (Al_2O_3)	0.33
Iron oxide (Fe_2O_3).....	0.47
Calcium carbonate.....	96.53
Magnesium carbonate	0.38
Phosphoric acid	trace
Soda and potash.....	trace
Sulphuric acid	trace
	99.67

The above figures computed to a basis of burned lime give the following:

	Per cent.
Insoluble matter	3.41
Alumina (Al_2O_3)	0.57
Iron oxide (Fe_2O_3)	0.82
Calcium oxide	94.53
Magnesium carbonate	0.66
	99.99

It may be seen that this lime contains very little iron oxide. It is evident therefore that we must look elsewhere for the sources of the iron which caused the trouble in the pan.

Some iron doubtless came from the lime, and some unquestionably came from the water used in diffusion. The water from the Leavitt well was found to contain 0.0024 per cent., or 24 parts per 100,000 of oxide of iron.

Quite recently a sample of lime removed from the kiln by Superintendent H. Schmöde was subjected to analysis and found to be radically different in composition from the first sample analyzed. The results of this analysis are here given:

	Per cent.
Acid-insoluble matter	26.10
Acid-soluble silica	0.26
Lime (CaO)	63.44
Magnesia (MgO)	0.11
Alumina (Al ₂ O ₃)	3.97
Iron oxide (Fe ₂ O ₃)	2.09
Carbon dioxide (CO ₂)	3.05
Sulphuric acid (SO ₃)	0.14
Undetermined	0.84
	<hr/> 100.00

There is certainly sufficient iron oxide shown in this sample to have caused all the disturbances noted. These two analyses would indicate a decided lack of uniformity of composition in the lime rock used at the factory.

To sum up the whole matter, it is my opinion that the coloring of the sugar in the massecuite was due to iron oxide. The source of this iron is still an open question, but the evidence at hand points rather clearly to the lime rock as the origin of it.

The author wishes to express his gratitude to Prof. H. H. Nicholson, as the investigation has been carried on in the chemical laboratory of the University of Nebraska by his permission.

SOME CHEMICAL CONSTANTS OF FOSSIL RESINS.¹

BY R. A. WORSTALL.

Received June 24, 1903.

WHILE the literature relating to the resins in general is quite extensive, it is nevertheless true that published data, in regard to

¹ Read before the International Congress of Applied Chemistry at Berlin, June, 1903.

the chemical constants of those fossil and semi-fossil resins which enter into the composition of varnishes, are quite scarce. Several investigators¹ have published results obtained from specimens of a few of these resins, but their results are in general of little or no value for various reasons. In the first place, many authors have not taken pains to properly classify the particular resins with which they were working. Then, too, their work has in many cases been with single specimens and not sufficient data are available for any one resin from which definite conclusions may be drawn. Last, but not least, as K. Dieterich has pointed out in his excellent book upon the analysis of resins,² the methods employed for resins in general have not been either accurate or uniform. Almost without exception the methods for the analysis of fats have been applied to the resins—a class of compounds entirely different from the fats in origin and constitution, so that we have ester values of resins which contain no esters, direct acid numbers which are far too low, and a general lack of concordance in the results.

It is chiefly due to Tschirch and his pupils that we have a clearer idea as to the origin and chemical constitution of the resins, while to K. Dieterich we owe quite as much from the analytical point of view. The later, in the book previously referred to, has given us suitable methods of analysis for each resin, and applied these methods in determining the constants of many species. The work herein recorded was undertaken to extend our information concerning the fossil and semi-fossil resins—the so-called "Copals"—a subject to which Dieterich has given but brief attention,—with the hope of developing a rational scheme of analysis. Each specimen was taken from large shipments, and represents a fair average sample of a definite commercial grade. As many different specimens as it was possible to secure were examined, in the belief that from a large number of data better conclusions could be drawn. As descriptions of the physical properties and characteristics of these various resins are to be found in several books treating of such subjects, it has seemed best to omit all such data from consideration in this article, giving for each resin no more description than is necessary to properly classify it.

KAURI COPAL.

Kauri resin, or Kauri copal, a semi-fossil, was originally an

¹ For a complete bibliography of this subject see "Die Harze und die Harzebehälter," by Tschirch.

² "Analyse der Harze, Balsame, und Gummiharze."

exudation from the pine tree of New Zealand—*Dammara Australis*—and is found only in the province of Auckland in open bush land from which the original forests have disappeared. In other parts of the colony, forests of these trees still exist which yield, on tapping, a soft spongy sap, while an intermediate quality of a semi-matured state—"bush Kauri"—also exists, which time might convert into semi-fossil variety. The data herein given refer entirely to the semi-fossil resin. The quantity of Kauri consumed annually in the United States more than equals that of all the other fossil and semi-fossil resins combined.

ACID NUMBERS.

In determining the acid numbers of Kauri the indirect method of Dieterich was followed, with a modification in the solvents used. One gram of the finely powdered resin was weighed out into a glass-stoppered bottle, and 15 cc. benzene and 5 cc. alcohol were added. Solution is complete in a few minutes with these solvents. Then 15 cc. of fifth-normal alcoholic potash were run in, the bottle tightly stoppered and allowed to stand eighteen hours, 25 cc. of alcohol then added and the excess of alkali titrated back with fifth-normal sulphuric acid, using phenolphthalein as an indicator. The method gives sharp end-reactions and closely agreeing duplicates. Blank determinations were run each time, using the same quantities of solvents.

As Dieterich has pointed out, direct titration gives acid values far too low for all resins, because the complete neutralization of the resin acids proceeds slowly. To illustrate this point the following experiment will serve. Several portions of a sample of Kauri, whose acid number had been accurately determined as 103, were weighed out and the acid number determined by indirect titration at different intervals of time. The results were as follows:

Time.	Acid number.
5 minutes	82
1 hour	92
3 hours	96
6 "	101
12 "	102
18 "	103

It is very necessary, as Dieterich has also observed, that rather strong acid be employed for the titration, as the addition of much

water hydrolyzes the potassium salts and lowers the apparent acid number. The author has found the addition of alcohol before the titration a great help in securing sharp end-reactions.

At the very beginning of this work it became evident that there was a wide divergence between the acid values of different samples of Kauri, ranging from a minimum of 72 to a maximum of 142, the large lumps ("bold" gum) having always the lowest acid values, the fine chips and dust the highest. Dieterich, who had noted with other resins, especially dammar, that the dust had much higher acid numbers than the large lumps, at once concluded that this must be due to adulteration of the dust with colophony. But as all the resins herein described were taken from original packages which had not been opened since leaving Auckland, the author was convinced that no adulteration was possible.

Dieterich has condemned the iodine and bromine numbers as of no value when applied to resins, and has omitted those determinations in his schemes of analysis. That he is entirely mistaken—at least in so far as the Copals are concerned—will appear from the following results. Proof that these Kauri samples were not adulterated was afforded at once when the iodine values were determined. The latter ranged from a maximum of 170 to a minimum of 74, the iodine value being always at a *maximum* when the acid number was at a *minimum*, and decreasing directly as the acid number increased. As colophony has an acid number of 160 and an iodine value of 170, adulteration with the latter would have caused a simultaneous increase in both acid and iodine values.

In determining the iodine value, the usual Hübl method was employed, using a large excess of iodine solution, and allowing to stand eighteen hours before titrating.

The following table shows the results obtained from forty-three specimens of Kauri resin.

Number.	Description.	Acid.	Iodine.
1.....	XXXX White, large lumps	72	170
2.....	XX Brown, " "	72	154
3.....	X White, " "	72	162
4.....	Brown one, " "	77	140
5.....	X Brown, " "	77	160
6.....	X Nubs, white, large	76	154
7.....	XX " " "	76	159
8.....	No. 1 " " "	85	146

Number.	Description.	Acid.	Iodine.
9.....	X Nubs, brown, large	87	148
10.....	No. 1 " white, "	87	144
11.....	No. 1 " " "	87	149
12.....	No. 1 " " "	91	142
13.....	Chips, white, large	80	153
14.....	" " "	82	159
15.....	" " "	79	151
16.....	" brown "	86	162
17.....	" light, medium	96	143
18.....	" " "	99	143
19.....	" " "	92	137
20.....	" " "	97	140
21.....	" " "	95	137
22.....	" brown, "	89	132
23.....	" light, small	112	115
24.....	" dark, "	113	110
25.....	" and dust	111	115
26.....	Small brown chips	92	124
27.....	Bright fine chips	103	120
28.....	" " "	103	125
29.....	" " "	107	113
30.....	" seeds	107	113
31.....	Medium "	103	113
32.....	" "	108	111
33.....	" "	122	105
34.....	" "	123	105
35.....	" "	122	107
36.....	Dark "	125	95
37.....	Bright dust	118	105
38.....	" "	120	105
39.....	Medium "	127	93
40.....	" "	130	87
41.....	" "	123	82
42.....	Brown "	133	89
43.....	" "	142	74

While no particular relation could be expected to exist between two arbitrary values such as the acid numbers and the iodine absorption, it is worth noting that the sum of these two values is approximately a constant. For the forty-three specimens the average of this sum is 228, the maximum being 248 and the minimum 205. And if for each specimen the percentage of impurities is taken into consideration and these values estimated for the pure resin contained, the divergence is less marked. In other words, the iodine number decreases in almost exact proportion as the acid number increases, and *vice versa*.

From the researches of Tschirch and his pupils, it appears that the copals consist of "resenes"—neutral compounds containing oxygen and possibly of aldehyde nature—and of the resin acids. Other investigators¹ have noted the fact that the copals will absorb oxygen, and evidently the increase in acid number and decrease in iodine absorption is due to oxidation of these "resenes," by contact with the air, to resin acids, and that heretofore the finer the particles of the resin and the more porous they are, the higher will be their acid number. That this increase in the acid number is actually due to oxidation, the following experiments will illustrate.

A number of samples of Kauri were selected, each one finely powdered, and its acid and iodine numbers determined. These samples were then left four months in open bottles exposed to the air, and the powdered resins stirred from time to time to promote oxidation. At the end of this time their constants were again determined with the following results:

Number.	Before oxidation.		After oxidation.		Acid. Increase.	Iodine. Decrease.
	Acid.	Iodine.	Acid.	Iodine.		
1	72	154	87	133	15	21
2	76	159	111	121	35	38
3	77	140	93	115	16	25
4	72	170	107	110	35	60
5	97	109	104	99	7	10
6	105	113	109	112	4	1

Samples 1, 2, 3 and 4 were hard, "bold" gum of highest quality, while samples 5 and 6 were of a soft, spongy, lowest grade Kauri, in which oxidation had already made much progress before the experiment was carried out.

This oxidation proceeds rapidly in presence of alkalis, so that open saponification with alcoholic caustic potash gives acid numbers that are much too high. Doubtless this fact, in connection with the impossibility of obtaining correct acid numbers by direct titration, has led to the reporting of ester values in resins where no esters exist. That Kauri is free from esters was shown by saponifying several samples in flasks with return condensers, digesting for one hour on the steam-bath. In every case the saponification number thus found was the same as the indirect acid number.

¹ See Kienastling, Weger, and Lippert: *Chem. Rev.*, 98, 1, 286; *Ztschr. angew. Chem.*, 98, 1, 1244.

MANILA COPAL.

This semi-fossil resin comes from the islands in the Malay Archipelago. Its botanical source is unknown. Commercially it is second to Kauri in the amount consumed each year in the United States for varnishes. Nineteen samples were taken from direct importations, the acid and the iodine values being determined by the same methods employed for Kauri, with the following results :

Number.	Description.	Acid.	Iodine.	Sum of acid and iodine.
1.....	Finest white, "bold"	146	148	294
2.....	Medium " "	167	128	295
3.....	" " "	175	132	307
4.....	Hard brown "bold"	176	131	307
5.....	White Nubs	165	135	300
6.....	Medium white Nubs	176	125	301
7.....	Amber Nubs	180	125	305
8.....	White chips	176	127	303
9.....	" " "	178	131	309
10.....	Medium chips	180	129	309
11.....	" " "	180	125	305
12.....	Amber chips	182	119	301
13.....	" " "	182	117	299
14.....	" " "	186	119	305
15.....	" " "	187	120	307
16.....	" " "	187	116	303
17.....	" " "	188	119	307
18.....	" " "	190	120	310
19.....	Dust	199	104	303

It will be noticed that the sum of the acid and the iodine values is in each case quite near the average, 304, and that the less marked increase in acid values as the size of the gum decreases indicates that oxidation by the air is not so rapid as in the case of Kauri. The effect of oxidation was determined just as for Kauri by allowing the finely powdered resin to stand in contact with the air for four months. The following table shows the results :

Number.	Description.	Before oxidation.		After oxidation.	
		Acid.	Iodine.	Acid.	Iodine.
1.....	Hard brown, "bold"	176	131	183	128
2.....	" white, "	142	148	146	144
3.....	White chips	186	119	189	113
4.....	Medium chips	180	125	191	112
5.....	" white, "bold"	175	132	178	122
6.....	" " "	167	133	178	128

Oxidation, therefore, does not proceed as rapidly or as far with Manila as with Kauri. Open saponification, however, gives too high results. Closed saponification gives the same figures as the indirect acid numbers, showing the absence of esters.

PONTIANAC COPAL.

One of the most recently exploited copals is the so-called "Pontianac," a semi-fossil from the Malay archipelago. In many ways it seems to be a connecting link between Kauri and Manila, not only in its physical characteristics, but also in its chemical constants. At present the consumption of the resin in the United States is in an experimental stage, and only two samples were available.

Number.	Description.	Before oxidation.		After oxidation.	
		Acid.	Iodine.	Acid.	Iodine.
1	Medium chips	135	142	153	104
2	Small "	143	119	157	102

It will be noted that its acid and iodine values lie between those of Kauri and Manila, and that it is more easily oxidized than Manila, but not so readily as Kauri. In its physical properties it more closely resembles Manila. It contains no esters.

SOUTH AFRICAN FOSSIL COPALS.

Zanzibar, Madagascar and Mozambique copals, the hardest and probably the most ancient of the fossil copals, are all found on the southeast coast of Africa. The botanical source of Zanzibar copal is probably the *trachylobium verrucosum*, and it is probable that the other two varieties of resin come from closely related species. Zanzibar is still of commercial importance, but Madagascar and Mozambique are but little used in the United States.

The acid numbers, iodine absorptions, and effect of oxidation were determined for these resins just as for those previously described.

Resin.	Description.	Before oxidation.		After oxidation.	
		Acid.	Iodine.	Acid.	Iodine.
Zanzibar	Prime white "sorts"	79	123	79	123
"	Amber chips	104	115	102	114
Mozambique	White "sorts"	80	136	107	108
Madagascar	Amber "sorts"	95	126	100	106

Zanzibar does not seem to be readily oxidized. None of these resins contained esters.

WEST AFRICAN FOSSIL COPALS.

Of the west African copals, the following were examined: "North Coast" or "Akra," red and white Angola, Congo and Benguela. The botanical source of these resins is not known positively. The following table gives the results:

Resin.	Description.	Before oxidation.		After oxidation.	
		Acid.	Iodine.	Acid.	Iodide.
North Coast	White, "bold"	108	143	127	109
" "	" "	109	143	125	122
" "	" "	116	140	137	116
Benguela	" "	139	142	161	121
Congo	" "	150	122	150	116
"	No. 2	152	122	153	109
Red Angola, select		143	130	142	115
White "	"	127	136	128	118

It may be remarked that the effect of oxidation upon all resin described in this paper was studied in the same manner as for Kauri, by leaving the finely powdered resin in contact with the air for four months. It is worth noting that while oxidation does not increase the acid numbers of Congo or the Angolas, it materially decreases the iodine absorption. The reason for this is not clear. None of these copals contain esters.

SIERRA LEONE COPAL.

Sierra Leone copal is the exudation from the bark of the *Copaifera Guibourtiana*, on the west coast of Africa. This tree flourishes in the elevated mountainous districts. The gum is gathered as an annual crop, thereby differing from most of the other varnish resins. The annual gathering takes place about the end of March, the bark being extensively cut and slashed, and the gum which flows from these incisions being afterwards collected. This resin hardens rapidly. The supply has been steadily decreasing and the cost, in consequence, rapidly increasing, so that Sierra Leone is not now used to a very great extent in the United States.

Two samples were examined with the following results:

Number.	Description.	Before oxidation.		After oxidation.	
		Acid.	Iodine.	Acid.	Iodine.
1.....	Finest select No. 1	118	105	116	105
2.....	No. 2 grade	114	102	116	108

It therefore appears that Sierra Leone is not readily oxidized. Hot saponification showed absence of esters.

BRAZILIAN COPAL.

Brazilian copal is a semi-fossil resin of uncertain botanical source from South America. Three samples were examined with the following results :

Number.	Description.	Before oxidation.		After oxidation.	
		Acid.	Iodine.	Acid.	Iodine.
1.....	Fine "bold" yellow	131	123	138	116
2.....	" " white	143	134	150	119
3.....	" " "	149	125	158	116

DAMAR.

While Damar is neither a fossil nor semi-fossil resin, and hence not strictly included under the title of this paper, its importance in varnish-making is such that it seems well to include it in consideration. The white damars used in the manufacture of varnish are commercially of three varieties—the Batavian from Java, and the Singapore and Padang from Sumatra. They are all exudations of *Dammara Orientalis*, the trees being cut periodically for the gum.

Eleven samples of white dammar were examined with the following results :

Number.	Description.	Acid.	Iodine.
1	Select Padang	24	116
2	" Singapore	55	104
3	" Batavian	24	124
4	No. 1 "	24	117
5	" 2 "	41	116
6	" 2 "	41	115
7	Batavian siftings	50	108
8	" "	50	107
9	" dust	51	104
10	" "	47	106
11	" "	50	103

The acid numbers were determined just as for all the preceding resins, using the same solvents. The decrease in the iodine absorption as the acid number increases shows that oxidation occurs with damar just as with the other resins. Hot, open saponification gives too high acid numbers for the same reason. Had Dieterich determined the iodine numbers of the damar dusts whose acid numbers he found high, he probably would not have concluded that the dusts were adulterated with colophony.

It would seem to the author that, in view of the results obtained, the value of the iodine absorption method as applied to the varnish resins is fully established. The almost universal tendency of the resins to oxidation when in contact with the air, as also brought out by this work, and the consequent wide range in acid and iodine values, makes it evident that chemical comparison of different samples of any resin are of value only when the samples to be compared are of the same general nature—in other words, it will not do to compare “bold” gum with “chips,” or “Nubs” with “dust,” for the reason that the finer the particles of gum, the farther the oxidation has progressed. But when it is desired, for the sake of greater accuracy, to supplement physical tests or inspection by chemical analysis, the author has found the following scheme of analysis accurate and reliable, *provided* it is used comparatively, that is, to test “dust” against “dust,” “chips” against “chips,” etc.

Moisture.—The resin is finely powdered and 1 gram dried for one hour at 110° C. on a watch crystal.

Insoluble Matter.—Two grams of the finely powdered resin are weighed out into a small beaker, and 25 cc. benzene and 10 cc. acetone added. Solution is complete for the softer resins in a few minutes, and slow for Zanzibar and the other harder resins. When necessary, solution of the latter may be effected in épi-chlorhydrin, aniline, or other more active solvent. When the solution is complete, allow to settle until clear, and decant the clear liquid, but *not* through the filter as it would clog the paper. Add more of the solvents to the residue in the beaker, and wash onto a filter-paper, previously washed out, the same solvents dried and weighed. Wash the residue clean, dry and weigh as total insoluble matter.

Ash.—Ignite paper and contents until white, and weigh residue as ash.

Insoluble Organic Matter.—The difference between the total insoluble matter and the ash represents the insoluble organic matter—bark and vegetable débris.

Indirect Acid Number.—Weigh out 1 gram of the finely powdered resin into a glass-stoppered bottle, add 15 cc. benzene, 5 cc. alcohol and 15 cc. fifth-normal alcoholic caustic potash. Allow to stand tightly stoppered for eighteen hours, add 25 cc. alcohol, a few drops phenolphthalein, and titrate back with fifth-normal

sulphuric acid. The number of milligrams of potassium hydroxide used represents the acid number.

Iodine Absorption.—Weigh out 0.2 gram of the finely powdered resin into a glass-stoppered bottle and add 10 cc. chloroform. Add 40-50 cc. of Hübl's iodine solution, allow to stand eighteen hours, then titrate back with thiosulphate.

Color.—Dissolve 10 grams of the resin in 100 cc. of a mixture of half benzene and half acetone, allow to stand in a 4-ounce oil vial until it has settled bright, then compare the colors of the clear solutions.

The above methods, when applied to the comparison of similar grades of the same resin, give surprisingly accurate results. Other things being equal, a higher percentage of insoluble organic matter, which would char in the kettle and darken the melt, or a higher acid number and lower iodine value, which would show more complete oxidation and hence indicate a more porous structure in the resin, or a darker color in solution, indicating a corresponding darker color when melted—these are the points which condemn a sample.

In conclusion, the author would state that he hopes soon to extend this investigation to the melted copals—especially to study the oxidation of the same, which may have important bearing on the durability of varnishes made from these resins.

CHICAGO VARNISH CO.,
CHICAGO, March, 1903.

ON THE RELATION OF THE SPECIFIC GRAVITY OF URINE TO THE SOLIDS PRESENT. SECOND PAPER.

BY J. H. LONG.

Received June 18, 1903.

SOME months ago¹ I gave the results of experiments carried out on the determination of the relation between the total solids of urine and the specific gravity at 25° C. A factor was found here corresponding to the coefficient of Haeser, but considerably larger than the number usually given, on account of the higher temperature at which the specific gravities were observed.

It seemed desirable to separate the effect of sodium chloride in fixing this relation, inasmuch as this substance is not a product

¹ This Journal, 28, 257.

of metabolism and is present in extremely variable amounts which have no relation to the urinary constituents of true metabolic origin. A new set of tests were therefore made in which the chlorine was accurately determined and calculated to sodium chloride. Then the specific gravities of correspondingly weak chloride solutions were found and these were subtracted from the observed specific gravities at 25° to find the specific gravity due to metabolic products. There are, of course, slight sources of error in this calculation, but they are not of great importance in the final result. In the first place, the chlorine is not always present as sodium chloride; sometimes there is more chlorine than the sodium will combine with, but the excess is never great. Secondly, the specific gravity of a mixed solution is not accurately equal to the sum of the factors for each component taken separately. The excess of the specific gravity over unity for the mixed solution is not exactly the sum of the excesses for solutions of the component substances taken separately in the same volume. But for the dilute solutions considered here the variations are not of material importance, and besides, this whole calculation is an arbitrary one which cannot lead to more than approximate results.

The determinations were made as described in the former paper and the coefficient or factor C was calculated by the expression

$$C = \frac{\text{Solids} - \text{NaCl}}{E_{\text{total}} - E_{\text{NaCl}}},$$

in which E_{total} represents the excess of the specific gravity of the urine over 1, and E_{NaCl} represents the excess of the specific gravity of salt solutions of the strength found over 1. The results obtained are given in the table.

No.	Solids per liter.	Sodium chloride per liter.	Specific gravity $\frac{25^{\circ}}{40^{\circ}}$	Sp. gr. of sodium chloride solution.	Coefficient for total solids.	Coefficient for solids less salt.
1	70.83	16.07	1.0287	1.0079	0.247	0.263
2	40.88	13.77	1.0169	1.0063	0.239	0.251
3	60.35	10.26	1.0233	1.0040	0.255	0.259
4	52.99	12.47	1.0190	1.0054	0.278	0.298
5	43.87	15.72	1.0184	1.0077	0.238	0.263
6	50.58	18.43	1.0216	1.0097	0.233	0.270
7	50.69	16.91	1.0217	1.0085	0.234	0.256
8	67.13	15.25	1.0275	1.0072	0.244	0.256
9	29.68	15.04	1.0131	1.0071	0.226	0.244
10	50.69	13.99	1.0217	1.0064	0.233	0.240
11	34.34	11.48	1.0130	1.0048	0.264	0.278
12	58.72	16.63	1.0234	1.0084	0.251	0.280

No.	Solids per liter.	Sodium chloride per liter.	Specific gravity $\frac{25^{\circ}}{4^{\circ}}$	Sp. gr. of sodium chloride solution.	Coefficient for total solids.	Coefficient for solids less salt.
13	63.79	13.87	1.0238	1.0065	0.267	0.288
14	65.43	15.51	1.0260	1.0076	0.251	0.271
15	56.77	13.65	1.0234	1.0062	0.243	0.251
16	61.50	15.19	1.0238	1.0072	0.259	0.278
17	44.34	13.56	1.0172	1.0062	0.258	0.280
18	51.52	17.64	1.0202	1.0092	0.255	0.308
19	59.96	18.97	1.0235	1.0102	0.255	0.306
20	40.09	11.55	1.0154	1.0048	0.263	0.269
21	58.92	15.13	1.0230	1.0071	0.256	0.275
22	52.18	14.64	1.0213	1.0069	0.245	0.261
23	52.99	10.25	1.0190	1.0040	0.278	0.285
24	55.03	15.24	1.0220	1.0073	0.250	0.257
Mean,	53.05	14.63	1.0211	1.0069	0.251	0.271

It will be observed that the coefficient for the total solids is 0.251 and slightly smaller than the mean value found before, 0.260. The coefficient for solids, less sodium chloride, is considerably larger and, contrary to expectations, is the mean of results which show wider variations than in the other case. Most of the individual results are, however, near the mean value and for certain classes of calculations, therefore, the coefficient may be used with only a small probable error. It will be noted that the urines tested showed a range of concentration between about 30 and 70 grams per liter of solids.

NORTHWESTERN UNIVERSITY,
CHICAGO, JUNE, 1903.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 69.]

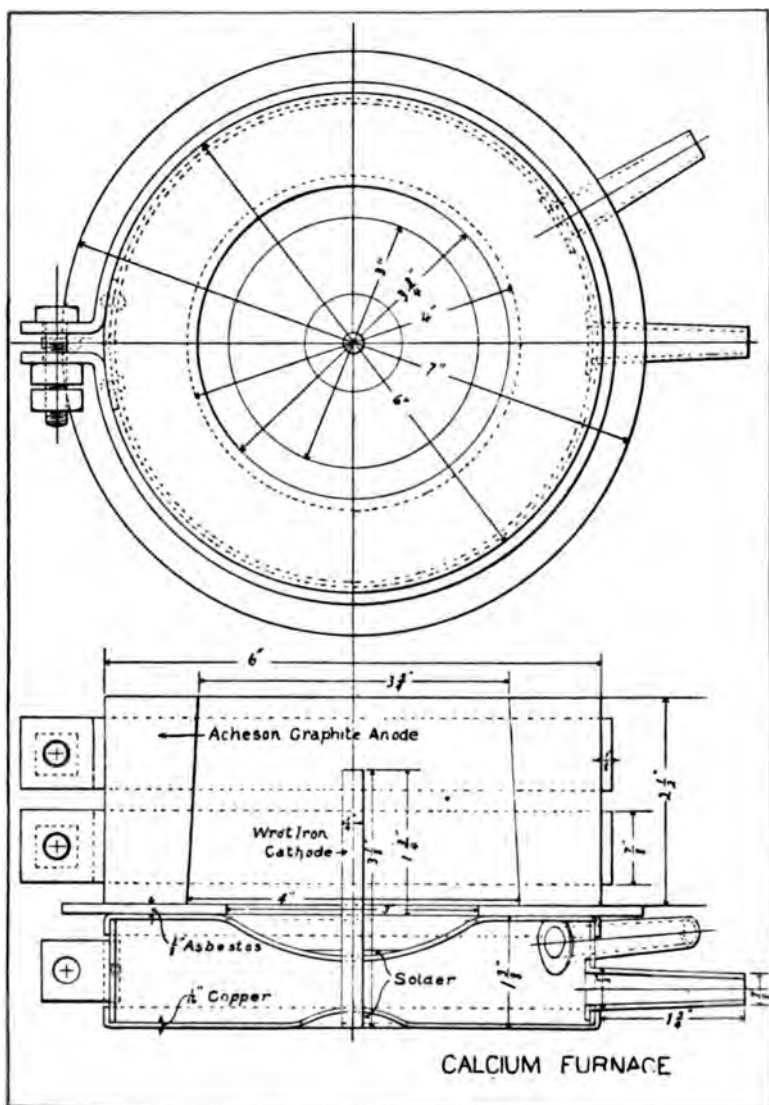
THE ELECTROLYTIC PRODUCTION OF CALCIUM.

BY JOSEPH H. GOODWIN.

Received June 26, 1903.

SEVERAL suggestions have been offered during the past year for the preparation of metallic calcium in the electrolytic way. The attempts made by the writer, with various furnaces, were fruitless. After much experimentation, the furnace, pictured below, was devised, and as it gave an excellent yield of metal it was thought that perhaps it would be helpful to others, hence this communication. Its construction is evident from the sketch. The

cathode of wrought iron is firmly fastened in electrical contact with a copper water-jacket, which serves as a cooler and as base for the furnace. Separated from this base by asbestos is a ring of graphite, made by boring out a 2.5-inch disk from a 6-inch Acheson graphite electrode. This ring constitutes the walls of the furnace and is also the anode, its electric connection being made by two wrought iron bands clamped firmly about it.



When the furnace has been arranged, spread powdered lime to the depth of half an inch over the bottom, pressing it down until it forms a firm, smooth floor. A stream of water is then sent through the jacket and the switch closed. Anhydrous calcium chloride, fused for half an hour in a wind furnace, is next poured into the furnace. It does not readily "wet" the graphite, it shrinks away from it; consequently a sheet of beautiful purple light separates the chloride from the graphite. It is an electric arc with a back electromotive force of 50 volts, which lowers the current. Contact between the chloride and graphite can be made by immersing a carbon rod along side the anode or by splashing the electrolyte against the graphite ring. The resistance should be cut out until a current of 100 amperes is passing. There will be a copious evolution of chlorine, for the removal of which a good "hood" is essential. Calcium chloride should be poured in from time to time, the temperature of the cell being kept at 950°. The liberated calcium melts from the iron rod upon which it has been deposited and floats to the surface, forming there a globule which, when about an inch in diameter, is removed with a small sheet-iron spoon.

The purity of the metal obtained in this manner varies with the purity of the chloride. Specimens made from chloride gotten from ordinary calcite showed, on analysis:

	Per cent.
Ca	94.80
Mg	4.16
Fe	1.03
	<hr/>
	99.99

The metal calcium is rather brittle. On a fractured surface it is more brilliant than steel, with a gray-white color. When cut or filed, it exhibits a yellow tinge, resembling German silver or gold alloyed with a great excess of silver. Globules of metal may be freed from chloride with alcohol and then ground on an emery wheel, when they become very bright. If preserved under petroleum, their metallic luster is retained.

Metallic calcium is quite stable. The red-hot, molten metal can be stirred about in the furnace quite vigorously, and even be dipped out and poured back without igniting. If, however, some of the metal be collected on a wire and struck smartly on the table, it will fly in all directions with a hissing sound and burn violently

with a blinding light. Similar energetic action takes place when the hot metal comes in contact with asbestos or with other reducible substances.

The attempts to prepare strontium were not very successful. It is quite probable that the furnace will have to be somewhat modified for this purpose and also for the isolation of barium.

UNIVERSITY OF PENNSYLVANIA.

NOTES.

The Preparation of Oxygen.—The action of dilute sulphuric acid on potassium permanganate affords a satisfactory method of making oxygen in small quantities. The possibilities are well known, but do not appear to have been utilized to that end except in connection with hydrogen peroxide.

The operation consists in heating gently a mixture of potassium permanganate and an excess of dilute sulphuric acid, in a generating flask provided with safety and delivery tubes. As this mixture begins to give off oxygen freely at 50°, very little heat is needed. The evolution of gas is continuous and quiet and under easy control.

The amount of oxygen to be obtained by this reaction is approximately represented by the equation



Ten grams of potassium permanganate (treated with 40-50 cc. of 1:4 sulphuric acid) give somewhat more than a liter of oxygen.

Convenient and safe, this method may be used to advantage in making oxygen for experimental purposes in courses in general chemistry.

R. B. RIGGS.

Note on the Effect of Combined Carbon in Iron on the Test for Tin.—A common test for tin depends on the reducing action of stannous chloride on mercuric chloride. If iron be used to reduce the tin, it should not contain any considerable amount of combined carbon, otherwise a counterfeit test may be obtained, no tin being present.

On making blank tests, it was found that, when the iron contained as much as 0.2 per cent. of combined carbon, its hydro-

chloric acid solution gave, with mercuric chloride, a very perceptible cloudy appearance in a few seconds. Some of the iron solutions yielded heavy precipitates at once.

The unsaturated hydrocarbons, liberated by the action of the acid on the iron carbides, seem to be the cause of this precipitation, and it is, roughly estimated, proportional to their odor. This odor is moreover destroyed by an excess of mercuric chloride, and further, if the solutions be previously heated until odorless, there is no precipitation.

Whatever be the cause, the action here is one of reduction and the precipitate formed is essentially mercurous chloride. Made in quantity, it was a dense, pure white, crystalline substance. When volatilized, a slight black residue generally remained. 0.8592 gram material gave 0.27 per cent. C. The action of such reagents as ammonium and potassium hydroxide, iodine and potassium iodide left no doubt as to its essential character, and a chlorine determination gave 14.93 per cent.; theory, 15.04 per cent.

In conclusion it may be said that, if the iron gives more than a faint "hydrocarbon odor" with hydrochloric acid, its solution will give a precipitate with mercuric chloride, and so interfere with the test for tin. Common wire nails may generally be used. Although their solutions have a reducing action, it is usually very slight and requires some time to develop sufficiently to be recognized.

R. B. RIGGS AND E. S. MERRIAM.

NEW BOOKS.

THE CHEMISTRY OF PIGMENTS. BY ERNEST J. PARRY AND JOHN H. COSTE. First edition, 1903. London: Scott, Greenwood & Co. New York: D. Van Nostrand Co. 275 pages, illustrated. Price, \$4.50 net.

This volume treats of the chemistry of pigments used for protective, decorative and artistic purposes. A brief introduction describes in a popular way the elements of the science of color, the spectrum and absorption spectra. In the second chapter are discussed the uses of pigments, the forms and combinations in which they are applied, and the mal-influence of air, moisture and gases on the paints. A number of tests are given that show the comparative resistance of the various paint-skins to these

agents, but there is no mention of the important precautions in applying the paint, etc., whose neglect so often results in unsatisfactory or contradictory deductions.

The following section deals with the inorganic pigments. Some eighteen pages are devoted to white lead and its manufacture. The authors adopt the theory of a chemical combination between white lead and linseed oil, a point that has been disputed by several investigators. The iron oxides, lead, chrome and copper compounds, and the carbon pigments are described in turn. Under the head of organic pigments are Prussian blue and the lakes of carmine, Brazilwood, and other animal and vegetable colors, and a number of the coal-tar dyes. An account of indigo and some minor organic pigments closes the volume.

The work can be commended for what it essays, to both the general reader and the chemist whose work is mainly in other departments. The space allotted to the description of the various pigments appears, on the whole, to be fairly well distributed, though the paragraphs on the vermillionettes, red lead and asphalt could have been amplified with advantage; on the other hand, the methods of chemical analysis of certain pigments might well have been omitted, since one competent to make such analyses always has access to detailed descriptions of the most recent and approved methods.

The book has a good index, and the print and binding are satisfactory.

FRANK JULIAN.

THE PRINCIPLES OF LEATHER MANUFACTURE. BY H. R. PROCTER, F.I.C., F.C.S. London: E. and F. N. Spon, Limited. New York: Spon and Chamberlain, 1903. xvi + 512 pp. Price, \$7.50.

The well known "Text-Book of Tanning," by the same author, having been long out of print, it was desirable to issue a revised edition which, however, takes the form of two books. The present volume contains a very satisfactory discussion of the principles on which the manufacture of leather is based, details of working processes being in the main excluded. Analytical processes and operations of chemical control for the tannery are found in the volume already published as the "Leather Industries Laboratory Book," a work now well known to chemists. To complete the series, a third volume, dealing with manufacturing processes, is desired.

In view of our very limited knowledge of the nature of the changes involved in leather-making, the author specifically points out the value, to the tanner, of practical experience and acquaintance with his material. There is a large amount of very useful information to the practical tanner in these pages: The effect on the leather, of the early treatment of the hide, such as drying, salting, etc.; the causes of injury to hides; the action of hard water in washing and soaking hides, and extracting tannin; the causes of swelling by dilute acids or alkalies, and the shrinking action of strong solutions; the nature of the changes produced in bating, puering and drenching, and the properties of the various materials used, are some of the points which are fully discussed.

Chrome tannage receives about eighteen pages of largely theoretical discussion, but the intelligent tanner, who has a little chemical knowledge, can pick out of this brief summary many bits of valuable information. The importance of this branch of the industry would seem to justify a somewhat more extended consideration.

The occurrence and properties of the vegetable tanning materials are fully described. The chapters on the grinding and extracting of tanning materials, and their analysis, and the chemistry of their action, contain many valuable hints. The chapter on dyes and dyeing is very satisfactory, while that on the construction of tanneries will furnish useful data to architects and builders who may be called on for this kind of work. The oil tannages and the properties of fats, soaps, waxes, etc., are all well considered; also the important items of evaporation, heating and drying; the disposal of wastes closes the text proper. Official methods of tanning analysis, both European and American, and a list of coal-tar colors suitable for use on leather, constitute the three appendices. Frequent foot-note references to original papers throughout the text add greatly to the convenience and value of the book.

Numerous illustrations are scattered throughout the book and the plates are noticeably clear and sharp, but some of the half-tone pictures from photographs are unsatisfactory; a comparison between Figs. 28, 29 and 42a, with Figs. 31 and 32, *e.g.*, leaves much to be desired in the former cases. The reference to Fig.

29 on page 223 is evidently a misprint, and the paragraph is somewhat obscure. The typography and general make-up of the book is good. The literature of tanning has long needed such a work as this.

The importance of technical education for tanners is now generally recognized, and the appearance of this work by one who is an acknowledged authority and leader in this educational movement, will doubtless further elevate the technical school in the estimation of successful tanners.

F. H. THORP.

THE PRAXIS OF URINARY ANALYSIS. A GUIDE TO THE CHEMICAL ANALYSIS OF URINE. BY DR. LASSAR-COHN. Authorized English translation by DR. H. W. F. LORENZ. New York : John Wiley and Sons. 1903. 58 pp. Price, \$1.00.

This little book is printed on very heavy paper, almost cardboard thickness, and heavily leaded to increase apparent size. It contains a few of the simplest qualitative reactions employed by physicians in the analysis of urine and directions for three quantitative determinations. These are so meager, however, that they are of no practical use. In addition to the urine tests, a few pages are devoted to the analysis of stomach contents. The amount of practical information contained in the book is so small that it can not be recommended to students or practitioners of medicine. The English of the translation is not always good.

J. H. LONG.

A TEXT-BOOK OF VOLUMETRIC ANALYSIS. With special reference to the volumetric processes of the pharmacopoeia of the United States. Designed for the use of pharmacists and pharmaceutical students. BY HENRY W. SCHIMPF, PH.G., M.D. New York : John Wiley and Sons. 1893. Fourth edition. 60 figures. 12mo. xxiii + 553 pp. Cloth. Price, \$2.50.

As the title suggests, this work is intended exclusively for the use of pharmacists, and its appearance in a fourth edition gives evidence that it meets a need of those for whom it is written to a greater degree, in some respects, at least, than any other available book. Its merit lies chiefly in the variety of methods offered, a direction in which most texts on the subject are deficient.

It is a collection of receipts for volumetric analysis and is almost wholly lacking in explanatory matter or in any exposition of the

reasons for doing things in one way rather than in another. The few explanations given are often inaccurate or positively incorrect. As an instance of this, the statement is made (p. 183) that sulphurous acid must be diluted to 0.04 per cent. before titrating it, "for if it is not sufficiently diluted there is risk of the sulphuric acid formed, being again reduced to sulphurous, with liberation of iodine, thus causing irregular results." This explanation has, of course, been exploded long ago. If true, it would mean that sulphuric acid of a dilution corresponding to 0.04 per cent. of sulphurous acid has an oxidizing action on potassium iodide and is reduced by it, a state of things which every chemist knows does not exist.

The directions are not always couched in the clear and pure English that one may properly expect to find in a text intended for student use; witness the following sentence taken at random from page 478. "Warm the mixture . . . and add . . . iodine solution from a burette until the brown color of the iodine solution is no longer decolorized and the mixture in the flask assumes a permanent, brownish yellow color, and upon shaking deposits a red-colored precipitate if much carbolic acid is present." Comment is unnecessary.

On the same page, the name of the well-known chemist Vortmann appears as "Wortmann," and the source of a paper which was published in the *Berichte* is given as "Pharm. Zeit. f. Russland." Perhaps it was Russian influence that changed the *V* to a *W*!

The method of titrating iodides by a mercuric chloride solution, due to Personne, is described without a word regarding the precautions which must be observed to obtain even tolerably correct results. The book shows throughout, with the exception of Chapter LXII relating to the determination of alkaloids, abundant evidence of being a compilation from other text-books rather than from original sources. The illustrations leave something to be desired, both as to execution and design. It seems to the reviewer scarcely necessary to introduce a cut of a liter-flask, unless some point regarding the model, etc., is to be elucidated. The picture of a liter-flask in the text bears the inscription "14.° R."!

LAUNCELOT W. ANDREWS.

ERRATA.

IN the paper by Albert P. Sy on "A New Test for the Stability of Nitrocellulose Powders," the following corrections should be inserted :

On page 565, *for* Fig. 7, *read* Fig. 10.

" " 567, line 5, *for* Fig. 1 *read* Fig. 10.

" " 567, *for* Fig. 8 *read* Fig. 7.

" " 568, *for* Fig. 9 *read* Fig. 8.

" " 568, *for* Fig. 10 *read* Fig. 9.

VOL. XXV.

[SEPTEMBER, 1903.]

No. 9.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 70.]

THE USE OF A MERCURY CATHODE IN ELECTROCHEMICAL ANALYSIS.

BY EDGAR F. SMITH.

Received June 26, 1903.

THE suggestion of precipitating metals in the form of amalgams was first made (1880) by Wolcott Gibbs,¹ who described a new scheme for the electrolytic determination of metals, before the National Academy of Sciences, in which scheme he recommended weighing out in a small beaker a definite amount of metallic mercury which was, by means of a platinum wire, connected with a battery and made the cathode, while in the salt solution, contained in the beaker, was suspended a strip of platinum, serving as the anode. The currents used varied greatly in strength. Salts of mercury, tin and cobalt were apparently decomposed, their respective metals being precipitated upon or in the mercury cathode. Quantitative results do not appear. The author of this method believed that possibly sodium and potassium might be separated in this manner and Professor Hunt remarked that the "process came with the beauty and force of a revelation."

¹ *Chem. News*, 42, 291.

Three years later (1883) Wolcott Gibbs¹ again directed attention to "the employment of mercury as negative electrode, the positive electrode being a plate of platinum. It was found possible to separate iron, cobalt, nickel, zinc, cadmium and copper so completely from solutions of the respective sulphates that no trace of metal could be detected in the liquid. the author had in view both the determination of the metal by the increase in weight of the mercury, and in particular cases of the molecule combined with the metal, either by direct titration or by known gravimetric methods." The experiments were purely qualitative, such being, in the author's opinion, sufficient to establish the correctness of the principle involved.

In 1886 Luckow,² cognizant of the difficulties attending the determination of zinc in the electrolytic way, described a course for this purpose which consisted in weighing out in a platinum dish a quantity of metallic mercury or its oxide, introducing the zinc salt solution and then electrolyzing, when the zinc, combined with the mercury, spread over the inner surface of the dish as a beautiful, adherent amalgam.

Nothing further was done towards the development of the ideas outlined in the preceding paragraph until 1891, when Vortmann³ described, at considerable length, the determination of several metals in the form of amalgams. His plan consisted in adding a weighed quantity of mercuric chloride to the solution of the salt to be electrolyzed, the metals being then precipitated together. The results were quite interesting and seemed to offer decided advantages, but later experience demonstrated that, except in a few cases, this method of analysis, as elaborated by Vortmann, was in nowise superior to the usual procedure in determining metals electrolytically.

A few months later, in the same year (1891), Drown and McKenna,⁴ striving to find a method suitable for the estimation of small amounts of aluminum in the presence of a preponderance of iron, had recourse to the suggestion of Wolcott Gibbs. They accordingly weighed a beaker containing a layer of mercury (the cathode), and introduced into the solution of the metals a platinum plate (the anode). The current was allowed to act through the

¹ *Am. Chem. J.*, 13, 571.

² *Chemiker-Zeitung*, 9, 338 and *Ztschr. anal. Chem.*, 25, 113.

³ *Ber. d. chem. Ges.*, 24, 2749.

⁴ *J. anal. Chem.*, 8, 627.

night and the iron was completely precipitated in the mercury. The aluminum remained in the slightly acidulated solution. These chemists encountered several difficulties in pursuing this course. The platinum wire projecting into the mercury often had iron precipitated upon it, so that it became necessary to weigh the wire, enclosed in a glass tube, together with the beaker of the mercury. Further, much annoyance was experienced in the efforts to dry the amalgam and obtain constant weights.

The preceding paragraphs comprise all that is to be found in the literature of electrochemical analysis, relating to amalgams and the use of mercury as a cathode in metal precipitations.

The thought of the writer had many times dwelt upon the facts mentioned above until at length it was determined to conduct a series of experiments with mercury as cathode, to establish two

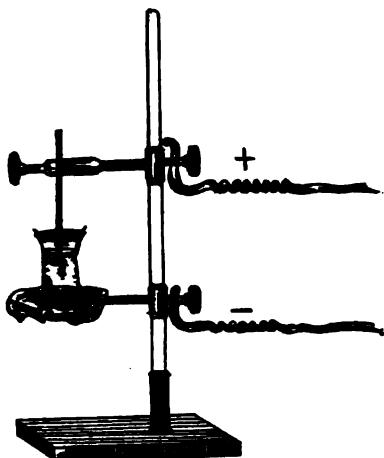


Fig. 1.

points: (a) The determination of the negative radical in various salts as well as the metals combined with them, and (b) the possibility of effecting the separation of certain metals.

To this end, practically the same device as that used by Drown and McKenna was adopted. Into the mercury, serving as cathode, there extended a glass tube from the lower end of which projected a carbon pencil, 1 mm. in length. This pencil of carbon was preferable to the platinum wire; metals did not adhere to it and, therefore, it was not necessary to weigh it together with the beaker and the mercury. The glass tube was nearly full of mer-

cury, into which dipped a copper wire connected with the negative binding-post. Such was the form of apparatus first used.

I. ELECTROLYSIS OF SULPHATES.

The sulphate first chosen was that of copper. A weighed amount of the salt was dissolved in water; the volume of its solution, when introduced into the apparatus mentioned above, equaled about 50 cc. It was electrolyzed at the normal temperature with the conditions given below. Sometimes during the electrolysis "copper trees" appeared on the surface of the mercury cathode (22 sq. cm. in area). They disappeared on gently shaking the beaker. This agitation was sufficient to make them amalgamate. When the liquid had become colorless, it was carefully siphoned into a beaker, its place being taken by distilled water. The washings accumulated in this manner equaled about 500 cc. The current was then interrupted. The sulphuric acid in the liquid conveyed away by the siphon was determined by titration with a tenth-normal sodium carbonate solution. The mercury cathode containing the copper was dried first with bibulous paper and then by standing for a number of hours over sulphuric acid, after which it was weighed.

Number.	Time.	Ampere.	Volts.	Cu present.	Cu found.	Cu present.	Cu found.	H ₂ SO ₄ present.	H ₂ SO ₄ found.	SO ₄ present.	SO ₄ found.
	Hours.	N.Dg.		Gram.	Gram.	Per cent.	Per cent.	Gram.	Gram.	Per cent.	Per cent.
1	5	0.02-0.10	2.25-5.0	0.1512	0.1495	25.30	25.02	0.2352	0.2355	38.55	38.50
2	3 ¼	0.08-0.12	4.25-5.5	0.1512	0.1499	25.30	25.08	0.2352	0.2347	38.55	38.47
3	4 ¼	0.08-0.12	3.5-4.0	0.3024	0.3002	25.30	25.11	0.4704	0.4694	38.55	38.47
4	4 ¼	0.10-0.13	4.0-4.5	0.3024	0.2986	25.30	25.00	0.4704	0.4723	38.55	38.80

The anode in Experiments 1, 2 and 3 was a strip of platinum foil, while in Experiment 4 it was a spiral of platinum.

It will be observed that, so far as the results are concerned, those relating to the metal fall below the theoretical requirement, while in the case of those bearing upon the acid they approximate theory more closely. Difficulty was experienced in drying the amalgam. Drown and McKenna had the same trouble. It seemed at first that it might prove detrimental to the general adoption of the method in ordinary analysis. It was, however, successfully overcome, for it was found that the amalgam could be washed with alcohol and ether, thus removing the final traces of water,

and that not more than fifteen minutes would then be necessary for the drying of the metal. A number of carefully conducted tests established this point. Mr. W. M. Howard of this laboratory also devised the following plan to eliminate the use of the anode of Drown and McKenna, as well as the carbon pencil.

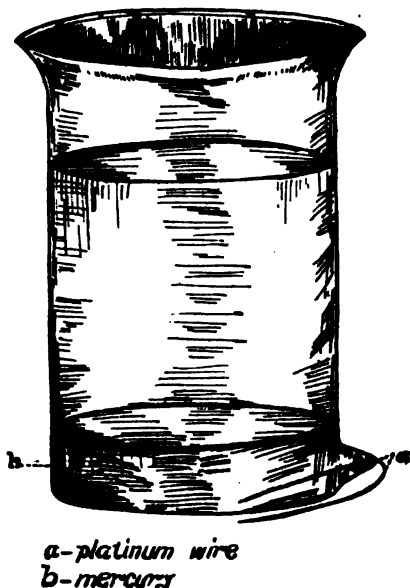


Fig. 2.

It is an extremely simple contrivance, consisting of a small beaker (50 cc. capacity), near the bottom of which there is introduced, through the side, a thin platinum wire. Internally it dips into the mercury, while externally it touches a disk of sheet-copper on which the beaker rests and which is connected with the negative electrode of a cell, thus making the mercury the cathode. By adopting this device and by washing the amalgam with alcohol and ether, the two chief disturbing factors were removed. Thus, on subsequently electrolyzing a copper sulphate solution containing 22.61 per cent. Cu and 41.20 per cent. SO_4 , there was obtained

(a)	21.61 per cent. Cu.....	41.23 per cent. SO_4 .
(b)	21.70 " " "	41.23 " " "

and on substituting a nickel sulphate solution, using a current of 0.05 to 0.06 ampere and 4 volts, the results were

30.41 per cent. Ni	50.75 per cent. SO ₄ .
30.40 " " "	50.76 " " "

while the theoretical requirements were

30.40 per cent. Ni	50.70 per cent. SO ₄ .
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With zinc sulphate, a current of 0.26 ampere and 6 volts acted for six hours, giving

(a) 24.27 per cent. Zn	36.71 per cent. SO ₄ .
(b) 24.37 " " "	36.61 " " "

while the quantities present were

24.30 per cent. Zn	36.60 per cent. SO ₄ .
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In sphalerite, the zinc determined volumetrically equaled 65.7 per cent., while a second portion of the same mineral rapidly decomposed with nitric acid and evaporated with hydrochloric acid, furnished a solution, which on electrolyzing with a mercury cathode showed 65.6 per cent. Zn.

In ferrous ammonium sulphate, electrolyzed in the same fashion, the following percentages of iron were found: 14.26, 14.28, 14.33, 14.19, 14.25 per cent., the theoretical being 14.28 per cent.

Additional data might be given to show that with a mercury cathode it is possible to electrolyze sulphates like those mentioned above and thus determine both the metals and the molecules with which they were in combination. It is needless to add that from such metals phosphoric acid, also, might be easily separated and determined in this way.

For quite a while the writer had been striving to effect, in the electrolytic way, the separation of iron from uranium. On observing the readiness and completeness of the precipitation of iron in the mercury, steps were at once taken to try this method in the hope of effecting the above separation. One-tenth of a gram of each metal was present in the solution in the form of sulphate. To this was added 0.25 cc. of 50 per cent. sulphuric acid and the liquid then electrolyzed with a current of 0.25 to 0.5 ampere and 6 to 8 volts for four and one-half to five hours. The iron was precipitated free from uranium. The separation was repeated several times with like satisfactory results. It may also be added that quantitative separations of iron from titanium, from zirconium and from thorium were made and the results were most satisfactory. In these separations the pressure did not exceed 5

volts with a cathode surface of 22 sq. cm. The precipitation of the iron was finished in five hours, although several trials were conducted through the night. The ordinary temperature prevailed in the separations. The quantity of each metal present was 0.1 gram. The found percentages of iron from titanium were 14.15, 14.20 and 14.21 per cent.; of iron from zirconium, 14.28 and 14.42 per cent.; of iron from thorium 14.31, 14.38 and 14.32 per cent., instead of the required 14.28 per cent.

II. THE ELECTROLYSIS OF METALLIC NITRATES.

Having ascertained that sulphates could be completely analyzed as indicated in the preceding paragraphs, it was only natural to turn to nitrates. Previous experience had taught that in such cases the acid radical instead of being released as such was reduced to ammonia. But this, it was believed, could be readily estimated if, before commencing the electrolysis of the nitrate, a definite volume of sulphuric acid of known strength should be added. When the electrolysis was finished, the free residual sulphuric acid could be titrated and the difference between its quantity and that originally introduced would give a difference which was combined with the ammonia. It would be a mere matter of calculation to arrive at the quantity of nitric acid previously combined with the metal. Guided by this thought a trial was instituted. The theoretical amount of metal was deposited in the mercury cathode, but upon titrating the sulphuric acid a volume of tenth-normal sodium carbonate equivalent to it was not only consumed, but in addition a volume sufficient to neutralize the nitric acid in union with the metal. In other words, the nitric acid had not been reduced to ammonia. It will be recalled that Vortmann¹ described a method for the determination of nitric acid which consisted in reducing the acid to ammonia in the presence of copper sulphate and sulphuric acid. This knowledge led to several repetitions of the experiment with like results, *vis.*, complete precipitation of the metal and liberation of the nitric acid. Nickel nitrate was the salt more particularly studied, although other nitrates showed a like behavior:

Nickel present. Per cent.	Nickel found. Per cent.	NO ₃ present. Per cent.	NO ₃ found. Per cent.
20.27	20.06	42.61	42.24
....	20.07	42.02
....	20.28	41.70
....	20.28

¹ *Ber. d. chem. Ges.*, 23, 2798.

These results were obtained with a current of 0.1 to 0.2 ampere and 3 to 3.5 volts. The time allowed was six hours. Search was made for ammonium salts but none were found, from all of which it would appear that the mercury cathode allowed of the complete determination of the acid and metal portions of nitrates, as well as of sulphates.

III. ELECTROLYSIS OF HALIDES.

Could the haloid acids be similarly determined? Several years ago Vortmann¹ published an account of the estimation of iodine in potassium iodide. Later Specketer² announced an electrolytic separation of the halogens. In neither instance was the estimation of the associated metal considered.

To begin, the writer set himself the problem of determining the sodium and the chlorine in ordinary salts. The small beaker, pictured on p. 887, was used. At first, silver-plated strips of platinum were made to serve as anodes. Very soon it was found that, as silver chloride was produced on these plates and loss took place in the drying of the same, anodes of platinum gauze coated with silver would answer better. It very shortly became evident that the chlorine was quantitatively deposited on these anodes. The method of procedure then became this: About 50 grams of pure mercury were put into the beaker, which was then weighed. The aqueous solution of a weighed amount of salt was introduced, the volume of liquid equaling about 40 cc. In this solution the weighed, silver-coated, platinum gauze was suspended. The current was then permitted to pass at the ordinary temperature. Almost immediately the silver began to darken in color from the lower edge of the gauze upwards. When this ceased, the decomposition was assumed to be at an end, whereupon the gauze was raised from the solution, rinsed with water and further washed with alcohol and ether. It was weighed after drying for a short time. For the gauze, a platinum spiral was substituted in the residual liquor in the beaker; the current was reversed, the layer of mercury being made the anode, when the sodium was rapidly driven into the water. All this occupied about twenty minutes, after which the alkaline liquor was titrated with standardized acid.

¹ *Ztschr. Electrochem.*, 1, 137; 2, 169.

² *Ztschr. Electrochem.*, 4, 539.

A solution of salt, containing 0.0606 gram of chlorine and 0.0390 gram of sodium, gave:

Number.	Cl. Gram.	Na. Gram.
1	0.0606	0.0389
2	0.0610	0.0384

Six hours were allowed for the decomposition. The current showed 0.0325 to 0.03 ampere and 2 volts.

On electrolyzing a solution of barium chloride, in the same way, there were obtained

Ba. Per cent.	Cl. Per cent.		Ba. Per cent.	Cl. Per cent.
55.87	28.69	instead of	56.14	29.09
56.07	29.31	

Strontium bromide was analyzed with just as much success. The same is true of other halides. Perhaps it may be well to add that both sodium chloride and barium chloride were electrolyzed successfully without the use of the mercury cathode. A flat, platinum spiral was made to take its place. The alkaline liquor, observing proper current conditions, did not interfere with the deposition of the halogen upon the silver gauze. The thought occurred that in this behavior there was a method of preparing caustic if only some other metal than silver could be applied as anode to take up the chlorine. Numerous experiments in this direction were made, but they resulted negatively.

In this work the writer had the aid of Messrs. William Blum, Raymond Wells, W. M. Howard, and Claude Poole, to each of whom his thanks are here expressed.

In conclusion it may be remarked that the hints which have been developed by this use of a mercury cathode are numerous. The separations of iron from uranium, titanium, zirconium and thorium point to other possibilities where this metal is separated with difficulty, more especially the rare earth metals. Further, there is a noticeable difference in the decomposition pressure of bromides of the alkaline earth metals, so that it would seem as if in a mixture of them this method would yield sharper determinations than we are by force of circumstances obliged to accept. The analysis of barium chloride or of common salt in the electrolytic way was not dreamed of in the years of the development of electrochemical analysis. In 1865 the metal copper was first determined electrolytically. Since then many other metals have been brought

into the circle of experimentation, but it is only now in the present—a period nearly forty years later—that interest is being taken in the determination of acidulous groups by the help of the current. To the writer, the possibilities that suggest themselves with other halides than those of the alkali and the alkaline earth metals seem great, and it is his hope that he may be permitted to continue studies in this direction for a little while longer.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 71.]

METAL SEPARATIONS IN THE ELECTROLYTIC WAY.

BY EDGAR F. SMITH.

Received June 26, 1903.

THE purpose of this communication is to submit the results obtained in trying to effect the separation of silver, mercury and copper from selenium and tellurium. These gaps in electrochemical analysis existed with two exceptions, *viz.*, silver from selenium, and copper from tellurium, and as the separations were needed both for practical reasons and also to extend and complete the possible range of applicability of the current in analysis, they were tried with evident success, as shown in the sequel.

SILVER FROM SELENIUM.

(a) *In Alkaline Cyanide Solution.*—In the *Zeitschrift für anorganische Chemie*, 31, 393 and This Journal, 25, 225, appeared Meyer's account of a method of determining the atomic weight of selenium, which consisted in electrolyzing silver selenite in cyanide solution. The results were so very concordant that there can be little question as to the completeness of the separation of the two metals. Working conditions were not given by Meyer, hence it was thought advisable to give those which in this laboratory proved very satisfactory for this particular separation. They appear in the following lines:

Silver present.....	0.1341 gram.
Sodium selenate present.....	0.2500 gram.
Potassium cyanide.....	3 grams.
Total dilution.....	150 cc.
N. D. ₁₀₀	0.02 ampere.
Pressure.....	2.5 volts.
Temperature.....	60° C.
Time.....	6 hours.
Silver found.....	0.1333 gram.

In another trial, with conditions like those just described, the silver which was precipitated weighed 0.1334 gram. These slight differences from the required amount of metal seemed to show that perhaps the current might well be increased toward the end of the experiment. This was done in two instances, from 0.03 ampere and 2.5 volts to 0.05 ampere and 3.5 volts. In consequence, the precipitated silver weighed 0.1340 gram instead of 0.1341 gram; further, the period of precipitation was reduced to three hours. The deposit of silver was pure white in color. The washing and drying were performed as so frequently mentioned in former accounts of silver determinations, and the details need not be given here.

(b) *In Nitric Acid Solution.*—The separation proving to be most satisfactory in an alkaline cyanide solution, the next step was to ascertain what would result in conducting it in the presence of an acid. The following conditions prevailed:

Silver present.....	0.1341 gram.
Sodium selenate present.....	0.2500 gram.
Nitric acid (sp. gr. 1.43)	1 cc.
Total dilution	150 cc.
N.D. ₁₀₀	0.015 ampere.
Pressure	1.25 to 2 volts.
Temperature	60° C.
Time.....	3 hours.

The silver deposit weighed 0.1342 gram. It was perfectly adherent and crystalline in appearance.

SILVER FROM TELLURIUM.

(a) *In Alkaline Cyanide Solution.*—It was believed that no difficulty would be met in making this separation with conditions similar to those pursued with silver from selenium in the same electrolyte. They were therefore tried. The precipitation of the silver proceeded very satisfactorily for an hour or more, then the deposit commenced to grow dark in color, and very soon black flakes appeared as a scum on the surface of the liquid and on the deposit as well. This behavior was always noticed, so that the efforts in this direction were abandoned. The attempt to separate mercury and copper from tellurium in cyanide solutions also resulted negatively. As will be observed below, their separation from selenium was most successful. By analogy, it would be expected that if silver, mercury and copper could be separated from

selenium in an alkaline cyanide bath, their separation from tellurium probably ought to follow as well under similar conditions. Here it did not. It is only another instance of cases where experiment alone can give the true answer.

(b) *In Nitric Acid Solution.*—

Silver present.....	0.1341 gram.
Sodium tellurate present	0.1344 gram.
Nitric acid (sp. gr. 1.43)	1 cc.
Dilution	150 cc.
N.D. ₁₀₀	0.01 to 0.015 ampere.
Pressure.....	1.25 to 2.0 volts.
Temperature	60° C.
Time.....	3 ½ hours.

The white crystalline deposit weighed 0.1344 gram.

In a second trial with like conditions the precipitated silver weighed 0.1341 gram.

MERCURY FROM SELENIUM.

(a) *In Alkaline Cyanide Solution.*—The example which follows demonstrated the applicability of the method:

Mercury present.....	0.1272 gram.
Sodium selenate present.....	0.2500 gram.
Potassium cyanide	1 gram.
Dilution.....	150 cc.
N.D. ₁₀₀	0.03 ampere.
Pressure	3 volts.
Temperature	60° C.
Time.....	5 to 6 hours.
Mercury found	0.1276 gram.

(b) *In Nitric Acid Solution.*—The conditions observed in the separation of silver from selenium will give most satisfactory results here.

MERCURY FROM TELLURIUM.

As previously observed, this electrolytic separation is not possible in an alkaline cyanide solution. It only remained, therefore, to ascertain whether it could be performed in a nitric acid solution. The trials were successful. One example will suffice to illustrate the most favorable conditions:

Mercury present	0.1272 gram.
Sodium tellurate present	0.2500 gram.
Nitric acid (sp. gr. 1.43)	3 cc.
Dilution.....	150 cc.

N.D. ₁₀₀	0.04 to 0.05 ampere.
Pressure	2 to 2.25 volts.
Temperature	60° C.
Time	5 hours.
Mercury found	0.1276 gram.

COPPER FROM SELENIUM.

(a) *In Alkaline Cyanide Solution.*—Two trials were made with conditions as follows:

Copper present	0.0745 gram.
Sodium selenate present	0.2500 gram.
Potassium cyanide	1 gram.
Dilution	150 cc.
N.D. ₁₀₀	0.2 ampere.
Pressure	3.5 to 4 volts.
Temperature	60° C.
Time	5 hours.
Copper found	{ (a) 0.0745 gram. (b) 0.0742 gram.

(b) *In Nitric Acid Solution.*—Just as in previous cases, all the results will not be given here. The conditions which proved most satisfactory were these:

Copper present	0.0745 gram.
Sodium selenate present	0.2500 gram.
Nitric acid (sp. gr. 1.43)	1 cc.
Dilution	150 cc.
N.D. ₁₀₀	0.05 to 0.08 ampere.
Pressure	2 to 2.5 volts.
Temperature	65° C.
Time	4 hours.
Copper found	{ (a) 0.0747 gram. (b) 0.0738 gram.

(c) *In Sulphuric Acid Solution.*—The quantities of copper and selenium present were the same as in the preceding separations. One cc. of concentrated sulphuric acid was added and the solution was electrolyzed with $N.D_{100} = 0.05$ to 0.10 ampere and 2 to 2.25 volts at a temperature of 65° C. The precipitated copper weighed 0.0743 gram instead of 0.0745 gram. The precipitation was finished in less than six hours.

COPPER FROM TELLURIUM.

The separation of these metals in cyanide solution, as already observed, failed. In nitric acid solution, they have been separated with perfect satisfaction.¹ It remained, therefore, to give the condi-

¹ Smith's "Electrochemical Analysis," 3rd edition, p. 134.

tions under which the two were separated with ease in the presence of sulphuric acid.

Copper present	0.0745 gram.
Sodium tellurate present	0.2000 gram.
Concentrated sulphuric acid	1 cc.
Dilution	150 cc.
N.D. ₁₀₀	0.05 to 0.1 ampere.
Pressure	2 to 2.25 volts.
Temperature	65° C.
Time	6 hours.
Copper found	{ (a) 0.0747 gram. (b) 0.0748 gram.

The writer has had the assistance of Mr. S. H. Ross in working out the details of these experiments, for which he would here acknowledge his indebtedness.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 72.]

THE RAPID PRECIPITATION OF METALS IN THE ELECTROLYTIC WAY.¹

BY FRANZ F. EXNER.

Received July 5, 1903.

SEVERAL years ago experiments were made in this laboratory looking to the electrolytic separation of molybdenum from tungsten. The anode was made to rotate by means of a small electric motor,² the idea being to use high currents with a high speed of rotation of the anode, thus hastening the deposition and, by agitation of the electrolyte, overcoming certain disturbances which had arisen. In the particular case referred to, the results were not entirely satisfactory. The idea, however, was shortly after tried upon other metals with success and led to the present investigation. Klobukow³ called attention to the agitation of the electrolyte, but never published any results. Gooch and Medway⁴ recently described successful experiments made with copper, nickel and silver solutions by *rotating the cathode*.

The purpose of the present investigation was to note the results

¹ From the author's thesis for the Ph.D. degree.

² Smith's "Electrochemical Analysis," p. 77, third edition, 1902.

³ *J. prakt. Chem.*, **33**, 475; **40**, 121.

⁴ *Am. J. Sci.* [4], **15**, 320.

following the *rapid rotation of the anode* and to develop with care the conditions for successful work, in various electrolytes,¹ for a number of metals. The result has been that many of them can now be precipitated quantitatively by the current in such astonishingly short periods that the methods of electrolysis are made more available to the analyst than heretofore. The essentials are recorded in the paragraphs which follow and the reader is referred to the author's thesis for greater details.

An ordinary platinum dish was used as cathode. The anode was a spiral of heavy platinum wire. It was 2 inches in diameter. Its center was depressed to give it the form of a shallow bowl. It was usually made to perform from 500 to 600 revolutions per minute. At higher speeds, the electrolyte is thrown against the cover-glasses; this is not objectionable, unless the dish contains too much liquid. The solution may sweep around the edge of the dish under the cover-glasses throughout the entire operation without any loss. The volume of liquid never exceeded 125 cc. and was not less than 110 cc. In every case the electrolyte was heated almost to boiling before exposing it to the action of the current. No external heat was applied during the electrolysis. The high currents kept the liquid hot. When the decomposition was finished, the rotator was stopped and the current was reduced by the introduction of resistance, water being added to cover the exposed metal, thus preventing its oxidation. The liquid in the dish was siphoned off, the dish being kept full by the addition of water from a wash-bottle. The metallic deposit was washed and dried in the customary way.

EXPERIMENTAL PART.

Copper.—This metal was precipitated from these solutions: A, sulphuric acid; B, nitric acid; C, ammonium sulphate and ammonia; D, ammonium nitrate and ammonia; E, potassium cyanide. The results were as follows:

No. of exp.	CuSO ₄ = Cu. Gram.	H ₂ SO ₄ dil. 1:10. cc.	A		Time. Minutes.	Deposited Cu. Gram.	Error. mg.
			Current N.D. ₁₀₀ = A.	V.			
1	0.4994	1	3	15	3	0.4992	0.2
			4	15	2		
			5	14-9	5		
2	"	1	5	"	5	0.4994	"
3	"	1	5	"	5	0.4994	"

¹ Consult Smith's "Electrochemical Analysis," 3rd edition, 1902.

² The brace indicates that all those current conditions were used in the experiment according to the time given.

B.

Conc. NH ₄ OH									
No. of exp.	CuSO ₄ = Cu. Gram.	Conc. HNO ₃ cc.	sol. cc. After 10 min.	Current N.D. ₁₀₀ = A.	V.	Time. Minutes.	De- posited Cu. Gram.	Error. mg.	
1	0.2484	1.0	5	10	10	0.2385	-9.9	
2	0.2484	1.0	5	10	15	0.2387	-9.7	
3	0.2484	1.0	5	10	20	0.2393	-9.1	
4	0.2484	0.5	{ 5	5	12	10	0.2482	-0.2	
				3	18	5			
5	0.2484	1.0	{ 5	5	10	10	0.2483	-0.1	
				5	12	5			
6	Identical with 5.								
7	0.4968	1.0	{ 5	5	8	10	0.4964	-0.4	
				5	10	5			

In Experiments 4 to 7, the electrolysis was first conducted for ten minutes in a nitric acid solution and then 5 cc. of concentrated ammonia water were added. This caused a change in the resistance of the solution, especially when only 0.5 cc. of nitric acid was used. The change was less marked when 1 cc. of the nitric acid was added, and since it also gave better results, that quantity is to be preferred. The deposit from this electrolyte was very satisfactory. It was dense, bright, and metallic in appearance.

C.

No. of exp.	CuSO ₄ = Cu. Gram.	(NH ₄) ₂ SO ₄ . Grams.	Conc. NH ₄ OH. cc.	N.D. ₁₀₀ = A.	V.	Time. Minutes.	Deposited Cu. Gram.	Error. mg.
1	0.2484	3	20	5	8	5	0.2488	+0.4
2	0.2484	1	20	5	12	5	0.2488	+0.4
3	0.4968	1.5	30	5	12	8	0.4966	—0.2

The conditions of 2 or 3 are preferable. The deposit is adherent. This electrolyte will be preferred, because in it the least time is required for complete precipitation.

D.

No. of exp.	CuSO ₄ = Cu. Gram.	NH ₄ NO ₃ . Grams.	Conc. NH ₄ OH solution.		Current cc. N.D. ₁₀₀ = A.	V.	Time. Minutes.	De- posited Cu. Gram.	Error. mg.
1	0.2484	3.0	20	5	8	10	0.2463	-2.1	
2	0.2484	1.0	20	5	12	10	0.2483	-0.1	
3	0.4968	1.5	30	5	12	15	0.4968	0.0	
4	0.4968	1.5	30	5	12	14	0.4964	-0.4	

The conditions of Experiments 2 and 3 are the most desirable. The deposits were excellent in character. A great advantage of this solution is, that in the ordinary course of analysis copper is usually obtained as nitrate. These conditions were made use of in the separation of copper from nickel.

E.

No. of exp.	$\text{CuSO}_4 = \text{Cu}$ Gram.	KCN.	Current $\text{N.D}_{100} =$ A.	V.	Time. Minutes.	Deposited Cu Gram.	Error. mg.
1	0.2484	Least possible for sol.	5	12	10	0.2136	-34.8
2	0.2484	"	6	18	10	0.2465	-1.9
3	0.2484	"	6	18	18	0.2479	-0.5
4	0.2484	"	6	18	18	0.2478	-0.6

The electrolyte yielded its last traces of copper very slowly, which was probably due to the solvent action of the solution upon the deposit. The deposits were of a golden red color and shone as if they had been polished.

NICKEL.

The solutions used in the following experiments were: A, ammonium sulphate and ammonia; B, acetic acid and ammonia; C, ammonium nitrate and ammonia; D, potassium cyanide.

A.

No. of exp.	$\text{NiSO}_4 = \text{Ni}$ Gram.	$(\text{NH}_4)_2\text{SO}_4$ Grams.	Conc. NH_4OH cc.	Current $\text{N.D}_{100} =$ A.	V.	Time. Minutes.	Deposited Ni Gram.	Error. mg.
1	0.2498	1.5	20	4	12	15	0.2496	-0.2
2	0.4996	1.5	30	5	10	15	0.4977	-1.9
3	0.4996	1.5	25	5	10	17	0.4998	+0.2

The conditions in 1 and 3 are the most desirable. The deposits were gray in color, dense, adherent and thoroughly satisfactory.

B.

No. of exp.	$\text{NiSO}_4 = \text{Ni}$ Gram.	30 % sol. $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$ cc.	Conc. NH_4OH cc.	Current $\text{N.D}_{100} =$ A.	V.	Time. Minutes.	Deposited Ni Gram.	Error. mg.
1	0.2498	10	10	5	8.0	10
2	0.2498	10	25	5	6.5	10	0.2498

The conditions in 2 were very satisfactory. The deposits were much like those from electrolyte A.

An experiment was performed in which 3 grams of ammonium nitrate were substituted for the acetic acid in Experiment B, 2; but after ten minutes no deposit had been formed. This suggested a possible separation from copper, which was worked out later. The experiments made with potassium cyanide were abandoned.

ZINC.

A solution of the sulphate was used. The dishes in which the precipitations were made were coated with silver. The electrolytes were: A, sodium acetate and acetic acid; B, sodium hydroxide; C, sodium hydroxide and potassium cyanide.

A.

No. of exp.	ZnSO ₄ = Zn Gram.	HC ₂ H ₃ O ₂ 30 per cent. solution.			Current N.D ₁₀₀ = A.	V.	Time. Minutes.	Deposited Zn. Gram.	Error. mg.
		NaC ₂ H ₃ O ₂ Grams.	cc.	ton.					
1	0.2502	1	0.2	3	18	10	0.2502	...	
2	0.2502	3	0.2	4	15	10	0.2502	-0.2	
3	0.5004	3	0.2	4	18	15	0.5001	-0.3	
4	0.5004	3	0.2	4	10	15	0.5002	-0.2	
5	0.5004	1	0.2	4	19	15	0.5000	-0.4	

Experiments 1 and 5 show that 1 gram of sodium acetate requires too high a voltage to overcome the resistance, causing an undue amount of heat. The high voltage in Experiment 3 was due to the great speed of rotation. The latter was reduced to 600 revolutions per minute in Experiment 4. The conditions in Experiment 2 and 4 are to be preferred, and gave very satisfactory results. The deposits were light gray in color, and crystalline.

B.

No. of exp.	ZnSO ₄ = Zn. Gram.	NaOH. Grams.	Current N.D ₁₀₀ = A.		V.	Time. Minutes.	Deposited Zn. Gram.	Error. mg.
1	0.5004	7	5	5	15	0.5003	-0.1	
2	0.5004	5	5	6	15	0.5003	-0.1	
3	0.5004	8	5	5	15	0.5004	...	
4	0.5004	12	5	5	15	0.5006	+0.2	

Nothing is gained by the extra sodium hydroxide in Experiment 4. The conditions of Experiment 3 were most satisfactory. The deposit from this electrolyte was sufficiently adherent for washing and weighing. C. Two experiments were made in which the zinc sulphate solution was precipitated by sodium hydroxide, the precipitate redissolved in potassium cyanide, and electrolyzed in the usual way, but it was finally found necessary to abandon this electrolyte.

SILVER.

The only electrolyte tried was the cyanide. A speed of 700 revolutions per minute was found to be most satisfactory.

No. of exp.	AgNO ₃ = Ag. Gram.	KCN. Grams.	Current N.D ₁₀₀ = A.		V.	Time. Minutes.	Deposited Ag. Gram.	Error. mg.
1	0.2495	2	2	5	7	0.2492	+0.2	
2	0.4990	2	2	5	10	0.4990	..	
3	0.4990	2	2	5	9	0.4992	+0.2	

The silver came down as a dense white deposit, excepting the last traces, which were a little loose, but quite adherent.

BISMUTH.

This metal proved most troublesome. The speed of rotation employed varied from 700 to 900 revolutions per minute. Electrolyte: 0.5510 gram of bismuth dissolved in a small excess of nitric acid and electrolyzed with a current $N.D_{100} = 1$ A. $V = 2.5$. Time = 18 minutes. The deposit of bismuth weighed 0.5507 gram. It was white and crystalline at first, but later it became black and loose, yet sufficiently adherent for washing and weighing.

Ten different electrolytes were tested with current strengths varying from 4 to 5 amperes, but all gave more unsatisfactory results than when nitric acid alone was present. The only electrolyte that gave deposits sufficiently satisfactory for analysis was that containing a small excess of nitric acid.

The suggestion of Vortmann was then applied, and the bismuth deposited with mercury as an amalgam. Solutions of mercurous nitrate and bismuth nitrate, each dissolved in the smallest excess of nitric acid, were used.

No. of exp.	$Bi(NO_3)_3 =$ Bi. Gram.	$HgNO_3 =$ Hg. Gram.	Conc. HNO_3 cc.	Current $N.D_{100} = A.$	V.	Time. Minutes.	Deposited Bi. Gram.	Error. mg.
1	0.2970	0.2920	..	4	12	15	0.2965	-0.5
2	0.2970	0.2920	..	4	12	12	0.2967	-0.3
3	0.2970	0.2920	1	5	8.5	8	0.2972	+0.2
4	0.2970	0.2920	1	5	8.5	8	0.2971	+0.1

The 1 cc. of nitric acid lowered the voltage and better results followed. The conditions of Experiments 3 and 4 are to be preferred. The deposit was iron-gray in color and very satisfactory.

MERCURY.

A solution of mercurous nitrate containing nitric acid was used. The speed of rotation was 700 revolutions per minute.

No. of exp.	$HgNO_3 =$ Hg. Gram.	Conc. HNO_3 cc.	Current $N.D_{100} = A.$	V.	Time. Minutes.	Deposited Hg. Gram.	Error. mg.
1	0.2920	1	4	11	15	0.2920	..
2	0.2920	1	7	12	5	0.2919	-0.1
3	0.5840	1	7	12	7	0.5837	-0.3

The deposits were perfect mirrors of pure mercury, and dissolved off the dish with great ease. The loss in weight of the dish in these three experiments was only 0.6 milligram.

COBALT.

A solution of cobalt sulphate was used. The speed of rotation

was 700 revolutions per minute. The electrolytes were: A, ammonium sulphate and ammonia; B, sodium and ammonium acetates and ammonia.

No. of exp.	CoSO ₄ =		(NH ₄) ₂ SO ₄ Grams.	Conc. NH ₄ OH sol. cc.	A.		Time. Minutes.	Deposited Co. Gram.	Error. mg.
	Co. Gram.				Current. N.D ₁₀₀ = A.	V.			
1	0.2460		3	50	5	10	15	0.2433	-2.7
2	0.2460		3	50	5	10	17	0.2440	-2.0

The solution from Experiment 2 gave no test for cobalt with ammonium sulphocarbonate, but there was a small deposit upon the anode. Experiments to remedy the defects of this electrolyte were not carried out.

No. of experiment.	CoSO ₄ = Co.		30 per cent. solution HC ₂ H ₃ O ₂ cc.	NaC ₂ H ₃ O ₂ Grams.	Concentrated NH ₄ OH. cc.	B.		Time. Minutes.	Deposited Co. Gram.	Error. mg.
	Co. Gram.					Current N.D ₁₀₀ = A.	V.			
1	0.2460		10	.	60	5	8	16	0.2404	5.6
2	0.2460		5	5	60	5	12 to 8	15	0.2462	+0.2
3	0.2460		.	2	60	5	15 to 12	15	0.2462	+0.2
4	0.2460		5	1	50	5	12 to 9	17	0.2459	-0.1
5	0.2460		5	1	50	5	10 to 7	15	0.2459	-0.1
6	0.4920		5	1	50	5	9 to 8	22	0.4916	-0.4
7	0.4920		5	1	50	5	9 to 8	22	0.4917	0-0.3

In Experiment 1 the deposit was excellent, but there was oxide on the anode.

The deposit in Experiment 2 was very good, but there was a slight discoloration of the anode.

The deposit of Experiment 3 was satisfactory. The anode was not coated.

The deposits in Experiments 4 to 7 were good. They were gray in color and quite metallic in appearance. The discoloration of the anode was so slight as to be negligible.

In the last three experiments, the speed was 500 revolutions per minute. These conditions are recommended. Sodium acetate hastens the deposit and prevents deposition upon the anode, while the ammonium acetate improves the deposit, but retards its formation.

CADMIUM.

The following electrolytes were used: A, sulphuric acid; B,

sodium acetate and potassium sulphate; C, potassium cyanide. The speed of rotation was about 600 revolutions per minute.

A.

No. of exp.	CdSO ₄ = Cd. Gram.	H ₂ SO ₄ dil. 1 : 10. cc.	Current N.D ₁₀₀ = A.	V.	Time. Minutes.	Deposited Cd Gram.	Error. mg.
1	0.2756	3	5	9	10	0.2756
2	0.2756	1	5	17-11	10	0.2755	-0.1
3	0.5512	1	5	8	15	0.5508	-0.4

Deposit 1 was crystalline at first, but the last portions of metal came down loose, but sufficiently adherent. Deposits 2 and 3 were beautifully crystalline and very satisfactory.

B, *Experiment 1*.—Electrolyte: Cd = 0.5512 gram. Sodium acetate = 2 grams. Potassium sulphate = 0.5 gram. Current N.D₁₀₀ = 5 A. V = 12. Time = 15 minutes. The deposited cadmium weighed 0.5514 gram. The potassium sulphate was added to increase the conductivity of the electrolyte.

Experiment 2.—Electrolyte: Cd = 0.5512 gram. It was precipitated with 0.5 gram of sodium hydroxide, the precipitate was dissolved with acetic acid, and 0.5 gram of potassium sulphate added. Current N.D₁₀₀ = 5 A. V = 11. Time = 15 minutes. Deposited Cd = 0.5514 gram.

C.

No. of exp.	CdSO ₄ = Cd. Gram.	NaOH. Grams.	KCN. Grams.	Current N.D ₁₀₀ = A.	V.	Time. Minutes.	Deposited Cd. Gram.	Error. mg.
1	0.5530	5	2	5	8	15	0.5531	+0.1
2	0.5530	5	2	5	8	10	0.5528	-0.2
3	0.5530	5	2	5	8	12	0.5528	-0.2
4	0.5530	5	2	5	8	10	0.5530

The deposits were white, compact and very satisfactory.

IRON.

A solution of ferric ammonium sulphate with ammonium oxalate was used as electrolyte. The speed of rotation was about 800 revolutions per minute.

No. of exp.	Ferric am. of alum = Fe. (NH ₄) ₂ C ₂ O ₄ . Grams.	H ₂ C ₂ O ₄ sat. sol. cc.	Current N.D ₁₀₀ = A.	V.	Time. Minutes.	Deposited Fe. Gram.	Error. mg.
1	0.2461	7	7	7.4	25	0.2458	-0.3
2	0.2461	7.5	7	7.5	25	0.2463	+0.2
3	0.2461	7.5	7	7.5	25	0.2461	..
4	0.4922	7.5	7	7.5	35	0.4922	..

The deposits were so dense and light in color that they resembled the polished platinum dish.

LEAD.

The metal was deposited as dioxide upon a dish which had its inner surface roughened by a sand blast. Over a gram of deposited dioxide showed no tendency to scale off. The speed of rotation was about 600 revolutions per minute. The only electrolyte used was nitric acid.

No. of exp.	Pb(NO ₃) ₂ = Pb. Gram.	HNO ₃ conc. cc.	Current N.D ₁₀₀ = A.	V.	Time. Minutes.	Deposited PbO ₂ Grams.	Error. mg.
1	0.2807	20	10	4.5	10	0.2804	-0.3
2	0.2807	20	10	4.5	10	0.2804	-0.3
3	0.5614	20	10	4.5	13	0.5613	-0.1
4	0.5614	20	10	4.5	13	0.5614
5	1.1228	20	10	4.5	15	1.1228

The deposits of lead dioxide were of a uniform, velvety black color.

No success was had with manganese.

MOLYBDENUM.

Electrolyte: A solution of sodium molybdate containing 0.2250 gram of molybdenum trioxide was placed in the dish, and to this were added 2 cc. of sulphuric acid (dilute 1 : 10), and 1 gram of potassium sulphate. The current N.D₁₀₀ = 4 A. V = 15. Time = 20 minutes. The molybdenum trioxide found weighed 0.2246 gram. The speed of the anode equaled 300 to 400 revolutions per minute.

TIN.

The electrolyte in this instance was a freshly prepared solution of stannous ammonium chloride, to which ammonium oxalate was added. The speed of the anode equaled 300 revolutions per minute.

No. of exp.	SnCl ₂ of 2NH ₄ Cl = Sn. Gram.	(NH ₄) ₂ C ₂ O ₄ hot sat. sol. cc.	Current N.D ₁₀₀ = A.	V.	Time. Minutes.	Deposited Sn. Grams.	Error. mg.
1	0.5396	100	5	5	13	0.5392	-0.4
2	0.2193	100	5	5.5	15	0.2193
3	0.2193	100	5	5.5	15	0.2191	-0.2
4	0.2193	100	5	5.5	15	0.2191	-0.2
5	0.2193	100	5	5.5	15	0.2193
6	0.4355	100	{ 5 8	{ 5.5 6.5	{ 15 ¹ 3	0.4353	-0.2
7	0.4355	100	{ 5 8	{ 5.5 6.5	{ 15 5	0.4355
8	1.0800	100	5	4.5	20	1.0801	+0.1

¹ In Experiments 6 and 7 the brace indicates two current conditions. The 5-A current running 15 minutes after which it was changed to 8-A.

GOLD.

The electrolyte was a solution of gold chloride to which potassium cyanide was added. The speed of rotation was about 500 revolutions per minute.

No. of exp.	AuCl ₃ = Au. Gram.	KCN. Grams.	Current N.D ₁₀₀ = A.	V.	Time. Minutes.	Deposited Au. Gram.	Error. mg.
1	0.0290	1.0	5	11	10	0.0289	0.1
2	0.0725	2.0	5	11	10	0.0725	...
3	0.1450	1.5	5	11	7	0.1447	-0.3

The deposits were excellent.

ANTIMONY.

Antimony chloride, with just enough hydrochloric acid to keep it in solution, was mixed with sodium hydroxide, sodium hydrosulphide and potassium cyanide, then electrolyzed as indicated below. The speed of rotation of the anode was 400 to 500 revolutions per minute.

No. of exp.	SbCl ₃ + HCl = Sb Gram.	NaOH 10% sol. cc.	NaHS. cc.	KCN. Grams.	Current N.D ₁₀₀ = A.	V.	Time. Minutes.	Deposited Sb. Gram.	Error. mg.
1	0.3042	30	20	2	5	4.5	20	0.3042	...
2	0.3042	30	20	2	5	4.5	20	0.3041	-0.1
3	0.3042	30	20	2	5	4.5	18	0.3041	-0.1

The deposits under these conditions were excellent. They showed a dense, light, metallic appearance. This is a new electrolyte for antimony.

No success was had with the deposition of arsenic.

SEPARATIONS.

SEPARATION OF COPPER FROM NICKEL.

The sulphates of the metals were used. The speed of rotation was about 600 revolutions per minute.

No. of experiment.	CuSO ₄ = Cu. Gram.	NiSO ₄ = Ni. Gram.	Concentrated HNO ₃ cc.	NH ₄ NO ₃ Grams.	Current N.D ₁₀₀ = A.	V.	Time. Minutes.	Deposited Cu. Gram.	Error. mg.
1	0.2457	0.25	0.25	3	4	5	15	0.2460	+0.3
2	0.2457	0.25	0.25	3	4	5	15	0.2458	+0.1

The deposits of copper were good and free from nickel. Several other experiments were performed in which more free nitric acid was used, and some in which less time was allowed, but in all of

them the precipitation was incomplete. The separation is probably possible, also, in an ammonia solution in the presence of ammonium nitrate.

Analysis of Nickel Coin.

A nickel coin, weighing 4.8514 grams, was dissolved in nitric acid, then evaporated on the water-bath, and the crystallized residue dissolved in water. Twenty-five cc. of this solution were placed in a weighed platinum dish and 3 grams of ammonium sulphate, and 1 gram of ammonium nitrate added. This solution was diluted with water to 125 cc., heated nearly to boiling and electrolyzed with a current of $N.D_{100} = 5$ A. $V = 5$. Time = 20 minutes. The precipitated copper weighed 0.3629 gram, equal to 74.81 per cent. of the coin. The solution from this deposit was precipitated with sodium hydroxide and bromine water, and the precipitate filtered, washed and dissolved in dilute sulphuric acid, containing 2.5 cc. of concentrated acid. To this solution 30 cc. of concentrated ammonia water were added, the whole diluted to 125 cc., heated, and electrolyzed with a current of $N.D_{100} = 6$ A. $V = 5$. Time = 17 minutes. The deposited nickel weighed 0.1185 gram, corresponding to 24.42 per cent. of the coin.

The attempt was next made to see how quickly a complete analysis of a nickel coin could be made. This was done as follows:

Weight of coin = 4.925 grams.

It was dissolved in 20 cc. of concentrated nitric acid diluted with an equal volume of water. When the solution was complete, the liquid was exactly neutralized with ammonia, transferred to a 250 cc. measuring flask and this filled with water to the mark. 25 cc. of this liquid were then transferred to a weighed platinum dish and 3 grams of ammonium sulphate were added. This was diluted to 125 cc., heated and electrolyzed with a current of $N.D_{100} = 5$ A. $V = 5.5$ for 20 minutes. The precipitated copper weighed 0.3691 gram = 74.95 per cent. of the coin. The solution from the copper was precipitated with sodium hydroxide and bromine water, filtered and washed. The precipitate was then dissolved in 2 cc. of concentrated sulphuric acid diluted with water, 30 cc. of concentrated ammonia water added, diluted to 125 cc., heated, and the solution electrolyzed with a current of $N.D_{100} = 6$ amperes and 5 volts. Twenty minutes were required for the deposition. The precipitated nickel weighed 0.1217 gram, corresponding to 24.71 per cent. The solution from the nickel deposit was

filtered, and the precipitate washed, ignited and weighed. The weight of ferric oxide was 0.0026 gram, which is equivalent to 0.35 per cent. of metallic iron. The total percentage equalled 100.01. The time required for the complete analysis was two and a half hours.

SEPARATION OF COPPER FROM ZINC.

The conditions which served for the separation of copper from nickel are applicable in its separation from zinc.

No. of exp.	CuSO ₄ = Cu. Gram.	ZnSO ₄ = Zn. Gram.	NH ₄ NO ₃ . Grams.	Conc. HNO ₃ . cc.	Current. N.D ₁₀₀ = A.	V.	Time. Min-utes.	Deposited Cu. Gram.	Error. mg.
1	0.2457	0.25	3	0.25	5	9	15	0.2458	+0.1
2	0.2457	0.25	3	0.25	5	9	15	0.2460	+0.3

This is sufficient to show the possibilities of this method of analysis. At the present time other separations are in progress.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 84.]

THE VOLUMETRIC DETERMINATION OF BISMUTH AS MOLYBDATE AND ITS SEPARATION FROM COPPER.¹

BY HERMAN S. RINDERER.

Received January 2, 1903.

At the present time the quantitative determination of bismuth is conducted in the great majority of cases by precipitation as bismuth basic carbonate by ammonium carbonate, in spite of the fact that many different schemes have been published for its separation from other metals and determination, using other reagents.

It was with the intention of finding, if possible, a reliable volumetric method equal in accuracy to the carbonate method, that this work was undertaken.

As the work progressed and the molybdate method was to be applied to ores, to show its practical value, it developed that a shorter and simpler separation of bismuth from copper, especially, would make the method complete from the ore, and it was then that the precipitation of bismuth with hydrogen sulphide from a solution containing tartaric acid and made alkaline with

¹ From author's thesis for the degree of Doctor of Philosophy. Read at the December meeting of New York Section of the American Chemical Society.

caustic potash and potassium cyanide was worked out and found satisfactory.

EXPERIMENTAL.

For the experimental part of this work a bismuth nitrate solution was prepared and standardized by the following methods: (a) Direct evaporation to dryness of a measured volume and ignition of the dry nitrate to trioxide; (b) precipitation of basic carbonate, drying and igniting to trioxide. The results obtained by these two methods were further checked by precipitating the bismuth as sulphide, and carefully igniting this to the trioxide (c).

(a) DIRECT EVAPORATION METHOD.

Bi(NO ₃) ₃ taken. cc.	Character of vessel used.	Found.	
		Bi ₂ O ₃ Gram.	Bi. Gram.
5	porcelain.	0.0643	0.05765
5	"	0.0643	0.05765
6	"	0.0773	0.06931
20	platinum	0.2578	0.23084
30	"	0.3663	0.34636

(b) CARBONATE METHOD.

Bi(NO ₃) ₃ taken. cc.	Found.	
	Bi ₂ O ₃ Gram.	Bi. Gram.
20	0.2581	0.23140
20	0.2577	0.23106
20	0.2570	0.23042
25	0.3222	0.28888
30	0.3869	0.34689
10	0.1288	0.11548
11	0.1415	0.12687
12	0.1542	0.13826

(c) SULPHIDE METHOD.

Bi(NO ₃) ₃ taken. cc.	Found.	
	Bi ₂ O ₃ Gram.	Bi. Gram.
20	0.2575	0.23086
20	0.2578	0.23114

From these results the strength of the solution was taken to be 1 cc. = 0.01155 gram bismuth.

ELECTROLYTIC METHODS.

It was deemed advisable to try some of the proposed methods

and that of Wimmenauer¹ looked promising. No satisfactory results could be obtained by it, however. Kammerer's² method was also tried with no better results, although Smith states in his book that it is probably the best of the proposed methods.

OXALATE METHODS.

Warwick and Kyle³ proposed, apparently as a new method, the precipitation of bismuth as oxalate either with ammonium oxalate or oxalic acid, and heating to facilitate the reaction. The clear solution is then decanted, and the precipitate is boiled with successive portions of water to convert the precipitate to the basic oxalate. This is then dissolved in acid and the oxalic acid is titrated with standard potassium permanganate solution. Both ammonium oxalate and oxalic acid precipitate bismuth as oxalate, which, however, is easily soluble in excess of ammonium oxalate whether hot or cold. Owing to this fact, ammonium oxalate was not further tried in determining the value of the proposed method. Oxalic acid was then tried as described by Warwick and Kyle.

It was noted that this is nearly an exact copy of Muir's method.⁴ The only great difference between them is that in Muir's method the precipitation is done in the cold, while Warwick and Kyle make their precipitation by heating, and also claim that two boilings with 50 cc. of water suffice to convert all the precipitate to the basic salt, while Muir says to boil with successive portions of water till the filtrates are free from acid. In the following experiments it was found that only very small amounts of oxalate could be converted by two boilings, while 0.0924 gram bismuth required three and four boilings with 80-100 cc. water to remove all free acid. The results in the following table were obtained by the factor calculated as given in the method by Warwick and Kyle. If 1 cc. of potassium permanganate equals 0.010 gram iron, it is equivalent to 0.0186 gram bismuth. One cc. of potassium permanganate used was equal to 0.005612 gram iron and hence equivalent to 0.01048 gram bismuth. This was the factor used. To show the irregularity of the results, the last column in the table shows what the factor for potassium permanganate to bismuth would be in each case according to the results obtained.

¹ *Zachr. anorg. Chem.*, 27, 1 (1901).

² "Electrochemical Analysis," Smith, 3rd edition (1902), p. 67; This Journal, 28, 83 (1903).

³ *Eng. and Min. J.*, April, 1901.

⁴ *J. Chem. Soc. (London)*, 33, 70 (1878).

RESULTS.

Bi(NO ₃) ₃ taken. cc.	Bi taken. Gram.	KMnO ₄ used. cc.	Bi found. Gram.	Calculated factors.
4	0.0451	3.8	0.0398	0.01186
6	0.0693	5.6	0.0587	0.01237
8	0.0924	8.4	0.0878	0.01100
10	0.1155	9.6	0.1006	0.01203
12	0.1386	12.4	0.1300	0.01117

These results being irregularly low, the cause was sought in the solubility of the oxalate. It was then found that the bismuth oxalate is slightly soluble in a hot solution containing oxalic acid. Apparently this fact was known to Muir, as in his method the bismuth is precipitated in the cold and the supernatant liquid is decanted. Then the precipitate, free from oxalic acid solution, is converted to the basic oxalate by boiling with water. The method was tried to ascertain its exactness so that it might be used for further standardization, if necessary. The results, however, were irregularly high, due to the difficulty experienced in converting to the basic salt. The precipitate is very fine and heavy and caused violent bumping. Four or more boilings were always necessary to free the washings from oxalic acid. The conversion had not even then been completed.

RESULTS.

Bi(NO ₃) ₃ taken. cc.	Bi taken. Gram.	KMnO ₄ used. cc.	Bi found. Gram.
4	0.0462	4.6	0.0482
6	0.0693	7.25	0.0775
8	0.0924	10.3	0.1079
10	0.1155	11.7	0.1226
12	0.1386	14.8	0.1551
14	0.1619	16.7	0.1750
8.1	0.0936	9.7	0.1016
9.9	0.1143	11.95	0.1252
4	0.0462	4.35	0.0456
6	0.0693	7.3	0.0765
14	0.1619	16.75	0.1755

In the last three determinations the precipitates were boiled several times after the conversion seemed to be complete, but the amount of oxalic acid retained was still higher than that calculated for the basic oxalate. The method did not seem practical for further work, as three other determinations started with these last three were lost by the violent bumping already mentioned.

Warwick and Kyle also claim that this method is a separation of bismuth from copper, arsenic, antimony and several other

metals. Copper being the most important, its behavior with ammonium oxalate and also oxalic acid was tried and it was found to act like bismuth in both cases, namely, it is soluble in excess of ammonium oxalate and insoluble in oxalic acid. After obtaining these results, it was not thought necessary to test the method of Warwick and Kyle further; as the principle of the method is old, the proposed changes render the method inaccurate, and the separations claimed are impossible.

These conclusions are further confirmed by Grabill,¹ who made a study of the reaction of bismuth with ammonium oxalate. He contradicts Warwick and Kyle, and also states that copper oxalate is insoluble.

Another proof that the separation of bismuth and copper is impossible by oxalic acid is given by the fact that Peters² precipitates copper quantitatively with this reagent and determines copper in this way.

THE MOLYBDATE METHOD.

When a solution of ammonium molybdate in nitric acid is added to a nitric acid solution of bismuth nitrate and the whole is neutralized with ammonia but not made alkaline, all the bismuth is precipitated as a molybdate in a fine flocculent form. If this is then warmed without boiling, the whole precipitate will collect into large, heavy flocks which settle very rapidly. This precipitate is easily washed by decantation and filters very rapidly. By the following work it was found that the molybdenum ratio to that of bismuth remains constant.

The limits of the precipitation are very narrow. The ammonium molybdate must be in large excess, three to four times the theoretical amount necessary for combining with all the bismuth. The original solution will contain about 5 per cent. of nitric acid, but this must be almost entirely neutralized with ammonia. To obtain this point, methyl orange is used as an indicator to get the solution neutral, and it is then acidified with 1 or 2 drops of 30 per cent. nitric acid. The whole is then heated on a thick asbestos pad over a small flame until the fine flocks have collected; generally the whole precipitate will rise from the bottom in large masses by the action of the hot circulating solution. The precipitate is then stirred to break it up, after which it is

¹ *Eng. and Min. J.*, 72, 354 (1901).

² *Ztschr. anorg. Chem.*, 26, 111 (1901).

allowed to settle. The precipitate is exceedingly heavy and settles in a few seconds, forming a compact mass. The supernatant liquid, which must be perfectly clear, is decanted through a plain filter-paper. Then the precipitate is washed twice by decantation with a 3 per cent. solution of ammonium sulphate, after which it is washed on the filter with the ammonium sulphate solution. It is then dissolved in dilute sulphuric acid and run through a Jones reductor with suction; after this, it is strongly acidified with sulphuric acid and is immediately titrated with standard potassium permanganate.¹

The precipitation and washing were done in a small beaker and the bulk was about 200 cc. It was found best to heat slowly, as with fast heating the solution was liable to come to a boil, which makes the determination unreliable. A 3 per cent. solution of ammonium sulphate was found satisfactory for washing and was preferred to any other salt as it has only constituents of the solution which is run through the reductor, and as ammonium sulphate is inactive to zinc in acid solution and also to potassium permanganate. A reductor with a column of zinc 40 to 45 cm. in length in a tube 1.25 cm. in diameter was used, to avoid the necessity of more than one passage through the zinc, and the suction flask was so large that the titration was made in it directly. Thus air had less chance of reoxidizing the molybdous oxide, which was to be determined by permanganate.

The color of the molybdate precipitate is pure white. Sometimes, when the conditions were not followed exactly, a slightly yellowish to canary-yellow compound resulted which gave varying results, but always lower than the white compound. This yellow molybdate, when formed, could however easily be changed to the white, by first making the solution alkaline with ammonia to throw down bismuth oxyhydrate, and then dissolving this in nitric acid. all this being done in the whole mixture of precipitate and solution. The clear solution is now re-treated as a new solution except that it is not always necessary to add more ammonium molybdate.

The results given in the following tables are calculated for the value in bismuth of 1 cc. of the potassium permanganate solution. To compare the results obtained in this way with an absolute standard, several samples of the purest obtainable bismuth were

¹ For further details of precipitation see the following paper.

weighed out and treated like the standard $\text{Bi}(\text{NO}_3)_3$ solution with very satisfactory results.

RESULTS.

$\text{Bi}(\text{NO}_3)_3$ taken. cc.	Bi taken. Gram.	KMnO_4 used. cc.	Equivalent amount of bismuth of 1 cc. KMnO_4 .
9	0.10395	28.5	0.003647
9	0.10395	28.7	0.003621
15	0.17325	47.75	0.003528
16	0.18480	50.9	0.003630
8.5	0.09818	27.	0.003636
12.3	0.14207	30.8	0.004610 ¹
7.8	0.09009	24.8	0.003632
9.8	0.11319	31.15	0.003633
11.6	0.13398	30.	0.004466 ¹

The results with the yellow precipitates indicate a totally different compound containing more bismuth than the white precipitate.

The following results were obtained with metallic bismuth:

Bismuth taken. Gram.	KMnO_4 used. cc.	Value of 1 cc.
0.1100	30.1	0.003654
0.1398	38.3	0.003626
0.1084	29.8	0.003637
0.1434	39.5	0.003630
0.1815	50.0	0.003630

From these results, the value of the potassium permanganate solution was taken as 1 cc. = 0.003630 gram of bismuth.

If the degree of reduction² of the molybdenum obtained in a Jones reductor is assumed to correspond to $\text{Mo}_{24}\text{O}_{37}$, the ratio of bismuth to molybdenum in the white precipitate is 1 : 1.977, while in the yellow precipitates it approaches 1 : 1.5, the ratio for the well-known normal bismuth molybdate.

The ratio was determined gravimetrically as follows: 10 cc. of the bismuth nitrate solution were precipitated as molybdate under the usual conditions. This was decomposed with ammonium sulphide, which precipitated bismuth sulphide and held the molybdenum sulphide in solution. The bismuth sulphide was dissolved with hot, dilute nitric acid, and the bismuth determined by the evaporation method (a) as a check on the completeness of precipitation by ammonium molybdate. The molybdenum solution was acidified, saturated with hydrogen sulphide and heated in boiling

¹ Yellow precipitates.

² The degree of reduction of the molybdenum and the ratio of bismuth to molybdenum in this precipitate are discussed in the following paper.

water in a pressure bottle. The sulphide was filtered in a weighed platinum, Gooch crucible, washed with dilute sulphuric acid and with alcohol, then ignited very carefully and the oxide MoO_3 weighed. The results were:

	A. Gram.	B. Gram.	C. Gram.
Bi_2O_3 found	0.1289	0.1285	0.1292
MoO_3 found	0.1058	0.1058	0.1057
Atomic ratios, Bi to Mo	1 : 1.985	1 : 1.99	1 : 1.982

These results were obtained on white precipitates; a yellowish precipitate analyzed in the same way gave a ratio of 1 : 1.71.

The ratio of bismuth and molybdenum in the compound having been found to be very nearly 1 : 2, it was evident that some other element or compound entered into the composition of the precipitate. It also showed that this molybdate was unknown in the literature, as the only molybdate of bismuth that could be found was the normal molybdate, ratio 2 : 3, a yellow compound soluble in 500 parts of water.¹ It was naturally supposed that ammonium was the missing factor in the compound, as no other base was employed. Attempts were made to obtain the molybdate pure and free from ammonium sulphate, so that the ammonia in combination could be determined. This was not found possible, as both water and 50 per cent. alcohol decomposed the compound, and no other available liquid could be found with which the ammonium sulphate could be washed out, leaving the pure molybdate behind. This peculiarity of the compound made it necessary to make an indirect determination for ammonia, by finding the total in the compound and combined as sulphate; then determining the sulphuric acid present and calculating its equivalent of ammonia; this subtracted from the total ammonia would give the ammonia in combination. A definite amount of bismuth was employed every time to avoid the necessity of determining this and the molybdenum in each portion.

The results did not check well, but showed conclusively that the precipitate contained ammonia, to the extent of about 1 molecule. Although these results are not sufficiently accurate to prove the formula, they show that the compound is a new bismuth ammonium molybdate with a ratio of bismuth to molybdenum very close to 1 : 2. The formula $\text{BiNH}_4 (\text{MoO}_4)_2$ would satisfy these facts.

It should be emphasized here that the precipitate is pure white;

¹ Storer's "Dictionary of Solubilities."

that if it is yellow it is undoubtedly contaminated by the normal molybdate, and that it is formed when the clear nitric acid solution containing an excess of molybdate is slowly neutralized with dilute ammonia, and then warmed but not boiled. As the conditions for this precipitation are narrow, and the degree of the reduction of molybdenum variable,¹ it is evident that care and strictly uniform conditions are essential to the success of the method.

THE SEPARATION OF BISMUTH AND COPPER.

The exactness of the molybdate method for bismuth having been proved, it was thought advisable to find a shorter separation from copper, so as to make the method of practical value, if possible. The ammonium carbonate method is a perfect separation, if it is repeated several times, in presence of large amounts of copper. Naturally this method is slow.

Pretzfeld,² in his new separation of mercury from copper, arsenic, and antimony by hydrogen sulphide in a potassium cyanide solution containing tartaric acid, found that, among a few other metals, bismuth also interferes; he did not, however, determine whether it was completely precipitated. A few experiments showed that all the bismuth was thrown out of solution by Pretzfeld's conditions; namely, the acid solution is neutralized with potassium cyanide after about 30 cc. of a saturated tartaric acid solution have been added; enough potassium cyanide must be added to dissolve any precipitate which may form, except bismuth sulphide thrown out by the sulphur in the cyanide. This alkaline solution is now saturated with hydrogen sulphide gas, and the bismuth sulphide is filtered out. The filtrate is colorless to light lemon-yellow. When copper was added to the bismuth solution and the above conditions were applied, the deep red color mentioned by Pretzfeld was present every time, in spite of the presence of tartaric acid.

When the bismuth copper mixture was first made alkaline with caustic potash, after adding tartaric acid, and potassium cyanide was added till the solution was clear, neither a red color appeared, nor was it necessary to use more than a small amount of potassium cyanide. The solution, even after saturation with hydrogen sulphide was never darker than a light lemon-yellow. The most important points were, however, that all the bismuth was precipi-

¹ See following article.

² Dissertation, "The Determination and Separation of Mercury," Columbia University, 1902. *This Journal*, 28, 205 (1903).

tated as sulphide in small bulk, all copper remained in solution and the filter-paper could be washed free from copper with potassium cyanide solution or pure water, and pure bismuth sulphide remained.

RESULTS.				
Bi(NO ₃) ₃ taken. cc.	Bi taken. Gram.	Cu. Gram.	Bi ₂ O ₃ found. Gram.	Bi found. Gram.
10	0.1155	0.5	0.1285	0.11521
10	0.1155	0.5	0.1287	0.11539
10	0.1155	1.0	0.1284	0.11512

The bismuth sulphide was dissolved in nitric acid, and then the bismuth was reprecipitated as basic carbonate which was ignited to oxide and weighed.

ANALYSIS OF BISMUTH ORES.

Two samples of bismuth ores containing iron, but free from copper, were obtained and these were used to show the exactness of the new method, as compared to the basic carbonate method.

From 0.3 gram to 0.5 gram of the richer ore were used for analysis and treated as follows: The ore was decomposed with nitric acid and was evaporated with sulphuric acid to fumes; after dilution, the residue was filtered off and re-treated with nitric and sulphuric acids as before. The filtrates were combined and diluted to about 750 cc. Then bismuth sulphide was precipitated with hydrogen sulphide and filtered out. For the carbonate method, this sulphide was dissolved in hot dilute nitric acid and precipitated by adding ammonia and ammonium carbonate, and heating. The precipitated basic carbonate was filtered, washed and ignited in a weighed porcelain crucible. To insure against any reduction of metal by the burning of the paper, the carbonate was dissolved through the paper, into the crucible, with hot dilute nitric acid.

For the molybdate method, the bismuth sulphide was also dissolved in nitric acid and this solution was treated with tartaric acid, potassium hydroxide, potassium cyanide and hydrogen sulphide, to free the bismuth of impurities which would interfere in the molybdate method. The pure bismuth sulphide was again dissolved in nitric acid, precipitated as molybdate, dissolved, reduced, and titrated. The following results show the comparative accuracy of the two methods.

RESULTS.

Ore taken. Gram.	Bi_2O_3 Gram.	Bi found. Gram.	Per cent.
0.5001	0.1096	0.0983	19.65
0.5004	0.1098	0.0984	19.67
0.5008	0.1098	0.0984	19.65
0.5009	0.1095	0.0982	19.60
Ore taken. Gram.	KMnO_4 used. ¹ cc.	Bi found. Gram.	Per cent.
0.5000	29.6	0.0987	19.74
0.3011	17.8	0.0594	19.71
0.3003	17.6	0.0589	19.61

The second ore was similar to the first. The same scheme of analysis was employed.

RESULTS.

Ore taken. Gram.	Bi_2O_3 Gram.	Bi found. Gram.	Per cent.
1.0002	0.0843	0.0756	7.55
0.7506	0.0620	0.0556	7.41
Ore taken. Gram.	KMnO_4 used. ¹ cc.	Bi found. Gram.	Per cent.
0.7505	17.0	0.0567	7.55
0.5008	11.4	0.0380	7.57

ANALYSIS OF COPPER MATTE CONTAINING BISMUTH.

At the time these analyses were under way, no matte containing bismuth was on hand, so a convenient amount of bismuthinite was mixed and ground up with a matte to make it about 0.5 per cent. to 0.6 per cent. bismuth. This was then analyzed by the two methods, as with the ores.

The method of procedure was similar to that employed in the ores, except that decomposition was effected with nitric and hydrochloric acids, no sulphuric acid being used. For the basic carbonate method the bismuth was precipitated alternately with hydrogen sulphide in acid solution and then with ammonium carbonate in ammoniacal solution to free the bismuth of iron and copper. Otherwise the methods were the same. It may be noted that only one precipitation was necessary for bismuth with hydrogen sulphide in the tartaric acid, potassium hydroxide, and potassium cyanide solution to obtain the bismuth free from copper. For one determination by the molybdate method, the standard permanganate solution was diluted to one-tenth the strength to reduce the error in titration, as the amount of bismuth was so small.

¹ Factor : 1 cc. KMnO_4 = 0.00335 gram Bi.

RESULTS.

Matte taken. Gram.	Bi_2O_3 found. Gram.	KMnO_4 used. cc.	Per cent.
2.2433	0.0134	...	0.597
2.5295	0.0164	...	0.648
2.0004	0.0126	...	0.565
2.2294	3.9	0.583
2.0032	3.25	0.541
2.0935	3.4	0.542
2.0020	34.2 $\frac{\text{standard}}{10}$	0.553

The molybdate method was applied to the matte in the most unsatisfactory way, as only small samples were used. When, however, enough sample is on hand, in case of a matte low in bismuth, it is advisable to take 5 grams to 10 grams or more to start with, as no difficulty will be experienced in separating the copper, and the quantity of bismuth will be enough for convenient handling by the molybdate method. Small amounts of bismuth are more difficult to precipitate as molybdate, and the titration is not as reliable when only a few cubic centimeters of potassium permanganate are employed.

CONCLUSIONS.

The method proposed by Warwick and Kyle is founded on an old principle and the changes made by them make it worthless.

Bismuth is completely precipitated by hydrogen sulphide from a solution treated as follows: Tartaric acid is added to the acid solution; it is then made alkaline with caustic potash, a slight excess of potassium cyanide is added and the solution is precipitated with hydrogen sulphide. Under these conditions copper will remain in the solution. Small amounts of bismuth are quickly and easily separated from large amounts of copper in this way.

Bismuth is completely precipitated as bismuth ammonium molybdate by ammonium molybdate in a solution just acid with nitric acid. This precipitate can be washed with a 3 per cent. ammonium sulphate solution, and used for the determination of bismuth by dissolving in sulphuric acid, reducing the molybdenum and reoxidizing with potassium permanganate as in the method for phosphorus.

This separation and determination give a method equal in accuracy to the basic carbonate method, while the time necessary, especially when large amounts of copper are present, is very much less.

This work was carried out under the direction of Professor Edmund H. Miller, and it is with great pleasure that I take this opportunity of thanking him for the counsel and kind encouragement which he extended to me throughout the research.

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November 1, 1902.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 85.]

ON THE REDUCTION OF MOLYBDENUM BY ZINC AND THE RATIO OF BISMUTH TO MOLYBDENUM IN BISMUTH AMMONIUM MOLYBDATE.

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Received June 24, 1903.

NUMEROUS investigations have been made on the reduction of molybdenum by zinc in a reductor. W. A. Noyes¹ and Frohman came to the conclusion that the reduction corresponded to a salt of the oxide Mo_2O_3 , provided that the air is displaced by carbon dioxide in the titrating flask. Blair² and Whitfield, however, although they followed Noyes and Frohman's conditions, could never attain a reduction equivalent to the oxide Mo_2O_3 , but almost invariably obtained reduction equivalent to an oxide, $\text{Mo}_{24}\text{O}_{37}$. Other investigators have either confirmed the results of Blair and Whitfield or come to the conclusion that the reduction did not proceed even as far as $\text{Mo}_{24}\text{O}_{37}$, but to a point corresponding to an oxide of the formula $\text{Mo}_{12}\text{O}_{19}$. Drown,³ however, by the use of 100-mesh zinc in a closed flask, has obtained a reduction corresponding to the oxide Mo_2O_3 .

It was the object of this work to study the extent of the reduction produced in a reductor when the conditions, such as the length of the column of zinc, the acidity, the temperature and the atmosphere were varied, and to see whether the oxide Mo_2O_3 could be reached (Part I). And also, when the conditions for a definite degree of reduction were obtained, to apply these to the confirmation of the ratio of bismuth to molybdenum in the new bismuth

¹ This Journal, 16, 553.

² *Ibid.*, 17, 747.

³ Blair's "Chemical Analysis of Iron," 4th edition. p. 99.

ammonium molybdate described by Riederer in the preceding article (Part II).

PART I.

About 6 liters of ammonium molybdate solution were made containing 10 grams of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 2\text{H}_2\text{O}$ per liter. This was standardized by precipitating as lead molybdate, giving the following values per cubic centimeter in grams of molybdic oxide, 0.008032 : 0.008034 : 0.008037 : 0.008026 : 0.008024; average, 0.008031.

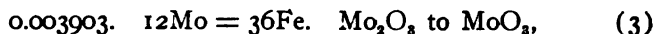
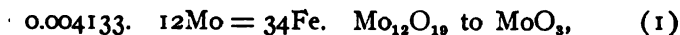
Neither conversion of the sulphide to oxide nor evaporation of the solution with nitric acid gave concordant results, so, to obtain a check by another method, Smith's electrolytic method was followed exactly, which gave for two determinations 0.008020 and 0.008035 gram of molybdic oxide per cubic centimeter, thus confirming the accuracy of the lead molybdate determinations.

A sufficient quantity of potassium permanganate solution was prepared and standardized both against ferrous ammonium sulphate and oxalic acid. The value was 0.004546 gram of iron per cubic centimeter.

According to the reactions



the value of this permanganate solution in grams of MoO_3 is



using the atomic weights of 1903, Fe, 55.9 and Mo, 96.

Experiment I.—An ordinary reductor was used with a 10-inch column of unamalgamated zinc (20-30 mesh); the bulk of the solution was 200 cc.; the acidity, 10 cc. concentrated sulphuric acid; the temperature, 75° C. The molybdate solution was followed immediately by 100 cc. of hot water and titrated at once in the reductor flask. The permanganate required for the iron in the zinc was deducted throughout. The time required for the solution to pass through the reductor was two minutes in this case.

The results were:

Ammonium molybdate. cc.	KMnO ₄ . cc.	MoO ₃ . Gram.	Value of KMnO ₄ per cc. in grams of MoO ₃ .
20	40.0	0.1606	0.004015
25	49.8	0.2007	0.004030
21	41.8	0.1687	0.004027

The results of this first experiment, though not very concordant, show an approximation to the value 0.004015 which corresponds to reduction equivalent to Mo₂₄O₃₇.

Experiment II.—Here and throughout the rest of the work a long glass tube, provided with a glass stop-cock, was used as a reductor. In this set of experiments, the length of the column of zinc was 15 inches; the time of passage 5-7 minutes; the temperature, 75° C.; the bulk of solution, 200 cc.; of wash water, 100 cc.; the acidity, 10 cc. of concentrated sulphuric acid.

The results were as follows:

Ammonium molybdate solution. cc.	KMnO ₄ . cc.	MoO ₃ . Gram.	Value of KMnO ₄ in grams of MoO ₃ .
20	40.00	0.1606	0.004015
22	44.10	0.1767	0.004007
12	24.28	0.0964	0.003970
21	42.20	0.1687	0.003998
20	40.00	0.1606	0.004015
20	40.20	0.1606	0.003995
20	40.12	0.1606	0.004003

Average, 0.0040004

With the longer time and the longer column of zinc, the results show a satisfactory agreement and that the reduction has proceeded slightly beyond Mo₂₄O₃₇. The factor for the MoO₃ standard calculated from these results is 0.88, the factor for phosphorus in the yellow precipitate 0.01579.

Similar experiments were made at a temperature of 25° C., with both a long and a short reductor, but the results were unreliable.

Experiment III. Reduction and Titration in an Atmosphere of Carbon Dioxide.—The apparatus consisted of a 500 cc. wide-mouthed bottle, fitted with a three-hole, rubber stopper. Through one hole the end of the reductor was passed, through the second the long tip of a burette, while the third was provided with a tube connecting with the suction. The procedure was as follows: The air in the reductor was first displaced by sucking a stream of carbon dioxide through it and then filled with air-free water to a height of 3 inches above the level of the zinc. Five grams of sodium bicarbonate were placed in the bottom of the bottle and then all the air replaced by carbon dioxide from a generator; then 5 cc.

of dilute sulphuric acid were poured in the bottle and the cork, containing the burette filled with permanganate and the reductor, fitted tight. The suction was turned on, and 100 cc. of hot, acidulated water (5 cc. of sulphuric acid in 100 cc.) passed through the reductor, followed immediately by the molybdate solution, and this in turn by 100 to 150 cc. of wash-water containing 3 cc. of sulphuric acid, taking care that the solution never went below the level of the zinc. When sufficient wash-water had passed through, the stop-cock of the reductor was turned off and the titration made at once. A blank was run and the iron in the zinc allowed for. The important conditions were: Time of passage, 7-10 minutes; temperature, 70°-75° C.; volume of molybdate solution, 200 cc.; acidity, 10 cc. concentrated sulphuric acid; length of column of zinc, 15 inches (not amalgamated). Results were:

Ammonium molybdate solution, cc.	KMnO ₄ , cc.	MoO ₃ , Gram.	Value of KMnO ₄ in grams of MoO ₃ .
25	51.00	0.2007	0.003935
26	53.15	0.2088	0.003928
20	40.70	0.1606	0.003946
20	40.60	0.1606	0.003955
21	42.80	0.1687	0.003941
25	50.90	0.2007	0.003943
19	38.80	0.1526	0.003933
20	40.70	0.1606	0.003946
20	40.65	0.1606	0.003951
25	50.90	0.2007	0.003943

Average, 0.003942

As the theoretical strength of the permanganate would be 0.003903 if the reduction were to Mo₂O₃, it is evident that this has not been attained, but that the reduction is to a point a little below midway between Mo₂₄O₃₇ and Mo₂O₃.

Experiment IV. Another Attempt to Reach Mo₂O₃.—The solution was first passed through a short reductor (Experiment I) and then was treated as in Experiment III, using an atmosphere of carbon dioxide, etc. Results were:

Ammonium molybdate, cc.	KMnO ₄ , cc.	MoO ₃ , Gram.	Value of 1 cc. KMnO ₄ in grams MoO ₃ .
25	51.10	0.2007	0.003927
26	53.18	0.2088	0.003926
20	40.93	0.1606	0.003921
21	42.95	0.1687	0.003951
19	38.85	0.1526	0.003951
18	36.76	0.1446	0.003933
23	46.97	0.1847	0.003932

Average, 0.003933

The volume at the first reduction was 100 cc., containing 5 cc.

concentrated sulphuric acid after passing the first reductor; it was made up to 200 cc. after 5 cc. more of sulphuric acid had been added. The time of passage was eight to ten minutes. The results do not differ sufficiently from those of Experiment III to deserve comment.

In order to test the rapidity of reoxidation by air, two more portions, each containing 0.1606 gram of molybdenum trioxide, were reduced, as just described, in an atmosphere of carbon dioxide, then before titration a blast of air was forced through, in one case for three, in the other for four minutes.

A. Blast for 3 minutes required 39.08 cc. KMnO_4 or 1 cc. = 0.004109.
B. " " 4 " " 38.50 " " 1 " = 0.004171.

Had there been no reoxidation, 40.83 cc. of KMnO_4 would have been required. The reoxidation to $\text{Mo}_{12}\text{O}_{10}$, equivalent to 0.004133, would have been accomplished in three and one-half minutes under those conditions.

Experiment V.—Identical with II except that amalgamated zinc was used. Results were:

Ammonium molybdate solution. cc.	KMnO_4 cc.	MoO_3 Gram.	Value of KMnO_4 in grams of MoO_3 .
20	39.9	0.1606	0.004027
25	49.9	0.2007	0.004022
21	42.0	0.1687	0.004016
20	40.0	0.1606	0.004015
26	51.9	0.2088	0.004023
23	46.0	0.1847	0.004015

Average, 0.0040196

The reduction does not proceed quite as far as with the un-amalgamated zinc, although the difference is hardly more than the experimental error. The average result is very close to reduction to Mo_2O_3 , while the three lowest and most concordant results agree exactly with the calculated value for that oxide—0.004015.

Experiment VI.—This is a repetition of IV, except that amalgamated zinc was used. The results were:

Ammonium molybdate. cc.	KMnO_4 cc.	MoO_3 Gram.	Value of KMnO_4 in grams of MoO_3 .
25	51.0	0.2007	0.003935
25	50.8	0.2007	0.003951
29	59.1	0.2329	0.003941
26	53.0	0.2088	0.003940
24	48.8	0.1927	0.003949
21	42.7	0.1687	0.003951
20	40.6	0.1606	0.003955
20	40.7	0.1606	0.003946
21	42.6	0.1687	0.003960

Average, 0.0039475

This is practically the same result as with the unamalgamated zinc, though here, as in the preceding experiment, there is a tendency for the amalgamated zinc to give a slightly less complete reduction.

Experiment VII.—Reduction with Zinc Foil in a Flask.—Twenty cc. of the standard ammonium molybdate solution were diluted to 100 cc. and placed in a flask with four pieces of thin sheet zinc, 1 inch square, and 15 cc. of sulphuric acid, and boiled for twenty minutes. The solution became deep green in color, but on dilution to 300 cc. with *cold* water it changed to port-wine color. The results were 39.1 cc. and 38.9 cc. of the permanganate solution, so that the reduction was very nearly equivalent to $\text{Mo}_{12}\text{O}_{19}$.

Average result, 1 cc. $\text{KMnO}_4 = 0.004118$.

Theory for $\text{Mo}_{12}\text{O}_{19}$, 1 cc. $\text{KMnO}_4 = 0.004133$.

The same experiments were repeated, except that the solution was boiled for half an hour and then diluted to 300 cc. with *hot*, air-free water. The solutions retained their deep green color and required 40 cc. and 40.15 cc. of permanganate for their reoxidation. These results are equivalent to 0.004015 gram MoO_3 and 0.004000 gram MoO_3 per cubic centimeter of permanganate, agreeing with reduction to $\text{Mo}_{24}\text{O}_{37}$, as obtained in Experiment II.

Magnesium and aluminum were also tried, but without satisfactory results.

Experiment VIII.—Blair's¹ conditions for the reduction of molybdenum were followed exactly. Twenty cc. of the ammonium molybdate solution was diluted to 150 cc., 20 cc. of sulphuric acid added and finally 5 grams of pulverized zinc. The solution was heated in order to start the reaction and then the stopper, containing a tube bent twice at right angles, was inserted. The other end of the tube dipped into a saturated solution of sodium bicarbonate. After complete solution of the zinc, which usually required about an hour, the green solution was immediately titrated with permanganate. Results were as follows:

KMnO_4 cc.	MoO_3 Gram.	Value of KMnO_4 in grams of MoO_3 .
41.5	0.1606	0.003870
41.3	0.1606	0.003888
41.6	0.1606	0.003861
41.4	0.1606	0.003879

Average, 0.0038745

¹ "Chemical Analysis of Iron," 3rd edition.

The calculated value for reduction to Mo_2O_3 is 0.003903. The results show that this reduction is fully obtained, but the method is not as satisfactory as the reductor.

CONCLUSIONS.

In general, we have confirmed Blair's statements in all respects and have not succeeded in obtaining reduction to Mo_2O_3 in a reductor. Our work has emphasized the importance of absolute uniformity in the conditions for both reduction and titration with with those used when the factor was obtained, as stated by W. A. Noyes. There is no definite stopping point at $\text{Mo}_{24}\text{O}_{37}$, though the reduction under the usual conditions proceeds very close to this point.

When the reduction is accomplished under the following conditions: Length of column of 20-30 mesh zinc, 15 inches; time of passage, about 6 minutes; temperature, 70° - 75° C.; volume, 200 cc.; acidity, 10 cc. of concentrated sulphuric acid; and the titration is made in the reductor flask without dilution or delay, but using no atmosphere of carbon dioxide, the factors are: For unamalgamated zinc, iron standard of permanganate times 0.88 gives MoO_3 standard; times 0.01579 gives phosphorus standard; when the "yellow precipitate" is titrated. For amalgamated zinc these factors are 0.8842 and 0.01586. The factors based on reduction to $\text{Mo}_{24}\text{O}_{37}$ are 0.8832 and 0.01584, using the atomic weights of 1903.

PART II.

Bismuth ammonium molybdate was prepared as follows: Ten cc. of the standard bismuth nitrate solution (described in the preceding article) were run into a beaker and 100 cc. of the ordinary acid ammonium molybdate reagent were added, the solution diluted to about 200 cc. and heated on an asbestos disk by a Bunsen burner. While the heating was in progress, ammonia (sp. gr. 0.96) was run in from a burette and the solution stirred vigorously. The addition of ammonia caused the formation of a precipitate and gave a yellow color to the solution which, as the neutral point was approached, disappeared, and a bluish tint was noticeable. This was used as an indication that sufficient ammonia had been added. The solution must be very hot, but not boiling, and the precipitate pure white. It was washed free from molybdenum by a 3 per cent. solution of ammonium sulphate, then into a

clean beaker with hot water. Ten cc. of sulphuric acid were added, and the solution was reduced and titrated under conditions of Experiment II. Assuming that there are present in the precipitate 2 molecules of MoO_3 for each atom of bismuth, the strength of the permanganate solution is 0.002896 gram bismuth per cubic centimeter. The results of three determinations were:

KMnO_4 cc.	Bi taken.	Bi found.	Calculated BiMo ratio.
39.60	0.1155	0.1147	1 : 1.986
39.75	0.1155	0.1151	1 : 1.993
39.70	0.1155	0.1150	1 : 1.991

The reduction and titration were then made according to the conditions of Experiment III; the bismuth value of the permanganate becomes 1 cc. = 0.002854. The results were:

KMnO_4 cc.	Bi taken.	Bi found.	Calculated BiMo ratio.
40.40	0.1155	0.1153	1 : 1.997
40.35	0.1155	0.11515	1 : 1.994

As methyl orange was not found a satisfactory indicator in the precipitation of bismuth by this method, others were tried and congo red was adopted as the most convenient. We next carried out the precipitation as follows: To the solution containing bismuth nitrate and 5 per cent. of free nitric acid, a decided excess of the ordinary molybdate reagent was added; there should be no precipitate produced at this point. A few drops of congo red were added and then very dilute ammonia slowly from a burette, with stirring; in a short time a white precipitate began to appear. We continued to add ammonia (in the cold) till the indicator became pink; next a few drops of dilute nitric acid were added so that the color was lilac (just neutral). The solution was warmed on a thick asbestos pad, but not to boiling. The precipitate collected and filtered well. It looked like silver chloride and was extremely easy to wash. The indicator was decomposed on heating and separated out as a pink lake, which adhered to the filter-paper.

Under the conditions given, the precipitation is absolutely complete, but if too much nitric acid is added, so that the indicator is turned back to a decided blue color, the precipitate does not collect or filter as well and the filtrate may contain traces of bismuth.

Two precipitates made in this way were analyzed as follows: After decomposition by ammonium sulphide, the bismuth sulphide was dissolved in nitric acid and weighed as oxide. The molybdenum was precipitated from the ammonium sulphide filtrate by

making slightly acid with hydrochloric acid and allowing to stand for several hours. The sulphide was dissolved in aqua regia, evaporated to small volume, neutralized with ammonia and then precipitated as lead molybdate. The results were:

No. 1.	Weight PbMoO_4	0.7558 gram	=	Mo	0.1977 gram.
	" Bi_2O_3	0.2456 gram	=	Bi	0.2202 gram.
	Atomic ratio			Bi : Mo	: : 1 : 1.95.
No. 2.	Weight PbMoO_4	0.6172 gram	Mo =	0.1615 gram.	
	" Bi_2O_3	0.1951 gram	Bi =	0.1747 gram.	
	Atomic ratio			Bi : Mo	: : 1 : 2.007.

Two portions of 10 cc. each of the standard bismuth solution were precipitated and the precipitates analyzed for ammonia. After deducting the relatively large amount present as ammonium sulphate, 0.0588 gram,¹ from the total ammonia, 0.06722 gram, the ammonia (NH_3) in combination with 0.1155 gram of bismuth was 0.0084 gram in one case, and 0.0598—0.05182 or 0.00806 gram in the other. These values give Bi : NH_3 ratios of 1 : 0.9- and 1 : 0.85 respectively or 4.24 and 4.06 per cent. $(\text{NH}_4)_2\text{O}$ compared with the theory for $\text{BiNH}_4(\text{MoO}_4)_2$, 4.76 per cent. Although these precipitates were sucked dry on a Büchner funnel to remove as much as possible of the excess of ammonium sulphate,² the relatively large quantity of ammonium as sulphate renders the accurate determination of that existing in combination with the bismuth a matter of difficulty.

The following experiments were made to see whether there was any variation in the composition of the precipitate when formed according to the three methods given. The results are in grams of bismuth, obtained by the titration method already fully described.

A. Riederer's conditions; methyl orange indicator; solution just acid with nitric acid; bismuth taken, 0.1280; found, 0.1278.

B. Congo red as indicator; solution neutral; bismuth taken, 0.1280; found, 0.1285 and 0.1288. (These slightly high results may be due to the carrying down of molybdenum by the indicator to form a lake.)

C. No indicator; solution made slightly alkaline; bismuth taken, 0.1280; found, 0.1274 and 0.1277.

CONCLUSION.

The peculiar properties of this precipitate,—that it cannot be

¹ Calculated from the SO_4 determined as BaSO_4 .

² As suggested by Professor W. A. Noyes.

washed with water or dried without decomposition, make the determination of its composition a matter of extraordinary difficulty, as everything must be found by ratios, and the ammonia determination is complicated by the ammonium sulphate present. But from the preceding determinations and others by other workers, there seems to be no doubt that the ratio of bismuth to molybdenum is as one is to two and that if the formula is not $\text{BiNH}_4(\text{MoO}_4)_2$, the variation is extremely slight and not such as to prevent the use of this precipitate for the volumetric determination of bismuth.

QUANTITATIVE LABORATORY,
JUNE 20, 1903.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE CONSTITUTION OF POTASSIUM RUTHENIUM NITROSO-CHLORIDE IN AQUEOUS SOLUTION.

BY S. C. LIND.

Received June 15, 1903.

THIS salt is the one which led Claus in 1845 to identify ruthenium as a new metallic element. He supposed it, however, to have the formula K_2RuCl_6 , and, therefore, to belong to the well-known class of salts represented by K_2PtCl_6 . In 1888, A. Joly¹ showed that this is not the case, but that the compound is a mononitroso salt of the formula $\text{K}_2\text{RuCl}_5\text{NO}$. The properties of this salt and analyses of it by several authors are presented in Freeny's "Encyclopedie Chimique."² J. L. Howe³ has confirmed this interesting discovery and has described the salt very fully, and given new analytical data in regard to it.

The properties presented by this salt, its rather unique formula, and also its relation to several other analogous ruthenium salts, have made a study of its constitution in aqueous solution of interest. Such an investigation was undertaken at the suggestion of Dr. Jas. L. Howe, to whom the author is indebted for the salt used in the following measurements. His analyses were made on this same sample; they will be found in his article referred to above. The author also desires to acknowledge his indebtedness

¹ *Compt. Rend.*, 107, 994 (1888).

² "Encyclopedie Chimique," III, 17, 1, 179-181.

³ This Journal, 16, 388 (1891).

to Dr. Arthur A. Noyes for his supervision of, and assistance in, this investigation.

The following determinations have been made. First, the electrical conductivity of the salt at 22°, at various concentrations from $1/20$ to $1/2560$ normal; second, the lowering produced by the salt in the freezing-point of water; third, the direction of the migration of the ruthenium during electrolysis.

I. CONDUCTIVITY MEASUREMENTS.

The apparatus used was the ordinary slide wire-bridge arrangement of Kohlrausch. The temperature employed was 22° (corrected), kept constant within 0.1° by means of a thermostat. The amount of salt required to make 100 cc. of an N/20 solution (that is, one containing $1/40$ K_2RuCl_5NO per liter) was dissolved in a weighed amount of water. This was used as a stock solution for making the more dilute solutions.

The salt was found to be perfectly stable in water solution at all the various concentrations, the conductivity of the solutions not changing at all in two weeks.

In the following table, the conductivity values obtained at the various dilutions, are given, expressed in reciprocal ohms. For comparison are also given the corresponding values for potassium platonic chloride at the same dilutions. These values were obtained from Walden's measurements at 25° by applying a temperature correction of 2.2 per cent. per degree, to the values for the different dilutions, obtained by interpolations from plots. The change from the Siemen's unit to the reciprocal ohm was effected by dividing each value by 1.063.

The specific conductivity of the water used in dissolving the salt and making the dilutions was 1.4×10^{-6} reciprocal ohms. This was subtracted in each case from the specific conductivity of the solution before calculating the equivalent conductivity.

TABLE I.—CONDUCTIVITY VALUES AT 22°.

Liters per equivalent.	Equivalent K_2RuCl_5NO .	Conductivity. K_2PtCl_6 .
20	99.8
40	106.4	96.6
80	110.3	101.5
160	115.4	105.4
320	118.5	108.5
640	121.9	111.1
1280	126.0	113.4
2560	127.5

II. FREEZING-POINT LOWERING.

The method employed was the usual one described by Raoult. A correction was applied to the observed lowering for the increased concentration of the solution by the ice separated from it. This correction was calculated from the heat of fusion and the supercooling of the solution, which was 1.5 to 3.5°.

TABLE II.—FREEZING-POINT LOWERING.

	Weight of solvent. Grams.	Weight of salt. Grams.	Liters per mol.	Observed lower- ing.	Corrected lower- ing.	Molecular lower- ing.	van't Hoff's coeffi- cient <i>i</i> .	Percentage dissoci- ation.
I.	20	0.4084	18.9	0.261°	0.251°	47.59	2.56	78.0
II.	20	0.4001	19.9	0.251°	0.242°	46.87	2.52	76.0
III.	20	0.2240	34.6	0.153°	0.148°	51.17	2.75	87.5
IV.	20	0.1052	73.4	0.071°	0.069°	50.59	2.72	86.0

By making a plot, using the conductivity values as abscissas and the cube roots of the corresponding concentrations as ordinates, a straight line is obtained. If this line be continued to zero concentration, a value is obtained for conductivity at infinite dilution, which in this case is found to be 133.5. This maximum conductivity of the salt represents its complete dissociation; therefore, from the ratio $\frac{\Lambda_{\infty}}{\Lambda_{\text{N/20}}}$, the percentage dissociation of the N/20 solution is found to be 74.7 per cent., slightly lower than the value found by the freezing-point method. From the above table, it appears that the salt is partially dissociated into *three ions*, as would be expected if we assign to it the formula $2\text{K/RuCl}_5\text{NO}$.

III. MIGRATION OF THE RUTHENIUM ION.

The solutions of this salt have a very characteristic violet-red color, which is due to the ruthenium ion. This seemed to offer a good opportunity of investigating the direction of motion of the colored ions under the influence of a direct electric current.

The form of apparatus used was suggested to the author by Mr. A. C. Melcher, and is so simple and so well adapted to experiments of this kind, that it may be briefly described.

A 2 per cent. solution of agar jelly in water was prepared, and to it was added a quantity of potassium chloride, sufficient to make an N/20 solution. Two 3-inch U-tubes were exactly filled with the jelly solution, which was then congealed by immersion in an

ice-bath. An approximately N/20 solution of the potassium ruthenium nitrosochloride was prepared in a small beaker. One arm of each of the two inverted U-tubes was dipped into this solution to a depth of about 6 mm. The other arm of one of the tubes was immersed in a beaker containing a hydrochloric acid solution, and that of the other tube into a similar beaker containing a caustic potash solution. Into these two beakers were introduced platinum electrodes, and a direct current was passed so that the *anode* was in the beaker containing the *acid* solution, and the cathode in that containing the alkaline solution. The purpose of these two solutions was to neutralize the products of electrolysis set free at the electrodes. Their concentration is immaterial.

A 110-volt current was then passed through the system. After its passage for a few minutes, a pink layer appeared above the surface of the solution, in the arm on the anode side, and moved steadily toward that electrode. This extension of the color zone continued regularly, with a well-defined and perfectly level boundary, at a rate of about 5 cm. per hour. On the other hand, in the cathode arm, not a trace of color appeared either above or below the surface of the solution.

This decisive result shows that the ruthenium is a constituent of the negative ion, and that there are no positive ions containing ruthenium in the solution. This consideration, together with the facts already shown in regard to the number of ions into which the salt dissociates, shows its structure to be $2K^+/RuCl_2NO^{--}$.

SUMMARY.

By way of summary, the following points in regard to the structure and properties of this salt may be mentioned, as having been established by the foregoing experiments.

(1) It is perfectly stable in aqueous solution, as is shown by the fact that its conductivity does not change at all in two weeks.

(2) It has a molecular conductivity very close to that of the analogous salt, potassium platonic chloride.

(3) The salt is partially dissociated into three ions as shown by its effect on the freezing-point of water. The value of van't Hoff's coefficient i , is 2.52-2.72 in $1/20$ - $1/70$ molar solution.

(4) The degree of dissociation of the salt, derived from the freezing-point lowering, agrees well with that obtained by conductivity measurements; it also agrees with the value for potassium platonic chloride.

(5) The direction of migration of the colored ions shows that the ruthenium is present in the negative ion, and in that alone.

(6) It will be seen from Table I, that the values for the ruthenium salt are uniformly about 10 per cent. greater than those for the platinum salt. It is evident, therefore, that the dissociation relations are entirely similar.

THE ACTION OF FUMING SULPHURIC ACID UPON ISO-AMYL CHLORIDE.

BY R. A. WORSTALL.

Received June 24, 1903.

SOME years ago, while the author was engaged upon an investigation of aliphatic sulphonics acids, some preliminary work was done upon the products of the reaction between isoamyl chloride and fuming sulphuric acid. It was the author's intention to make an extended study of the action of sulphuric acid of various degrees of concentration upon different alkyl haloids, but owing to pressure of other work this investigation was dropped, and neither the opportunity nor the facilities have since been available for completing this work. As it does not seem probable that opportunity will be afforded for any further work along this line, it may not be amiss to publish the results of the investigation so far as it was carried.

The following is a brief résumé of the literature upon the subject of the reactions between sulphuric acid and alkyl haloids. Williamson,¹ by the action of sulphuric anhydride upon ethyl chloride, obtained chlorethyl sulphuric acid, a heavy oil, decomposed by water into hydrochloric acid, sulphuric acid and ethyl sulphuric acid. Methyl chloride gave a similar result. By the action of chlorsulphuric acid upon the alcohols, the same compounds resulted.

Oppenheim² states that amyl chloride with concentrated sulphuric acid gave amyl sulphuric acid, and that all alkyl chlorides, by similar treatment, lose hydrochloric acid and form alkyl sulphuric acids. The same author,³ by acting upon ethylene chloride and its homologues with concentrated sulphuric acid in sealed

¹ *J. prakt. Chem.*, 73, 73.

² *Am. Chem. J.*, 6, 353.

³ *Ber. d. chem. Ges.*, 2, 212.

tubes at 130° C., obtained decomposition into carbon, sulphur dioxide and hydrochloric acid. No action was apparent at ordinary temperatures.

Wroblewsky¹ found that sulphuric anhydride with ethylene bromide separated bromine and hydrobromic acid and gave brom-

ethyl sulphonic acid, $C_2H_5 \begin{matrix} \swarrow Br \\ \searrow SO_3OH \end{matrix}$, from which the barium salt

was obtained. Ethyl iodide with sulphuric anhydride gave ethyl sulphonic acid.

Purgold,² by the action of sulphuric anhydride on ethyl chloride, obtained chlorethyl sulphate, chlorethyl sulphonic acid, and oxyethyl sulphonchloride. Armstrong³ studied the action of sulphuric anhydride on chloroform, carbon tetrachloride and carbon hexachloride, obtaining chlorcarbonic and chloresulphuric acids.

For the sulphonation of amyl chloride, 30 grams of isoamyl chloride were added gradually to 60 grams fuming sulphuric acid, and the mixture kept cool. Heat was generated with slight evolution of sulphur dioxide. When the reaction was complete, the solution was poured into water and the milky liquid extracted three times with ether. The acid solution was neutralized with barium carbonate and filtered. The filtrate was evaporated to dryness. A white salt was left, which was very deliquescent and which darkened somewhat at the temperature of the steam-bath. The salt was extracted with hot 90 per cent. alcohol and filtered. A large excess of ether in the filtrate precipitated a flocculent, white barium salt, the precipitation not being complete. This salt was analyzed after washing with ether and drying, and found to be impure, containing barium chloride.

The sulphonation was repeated, using 50 grams of isoamyl chloride and 200 grams of fuming sulphuric acid. The reaction mixture was poured into water and this solution extracted three times with ether. The ether solution was washed and evaporated. The residue of 12 grams was a red, oily liquid of a disagreeable odor, and was not further investigated. The water solution was neutralized with barium carbonate, filtered, the filtrate evaporated to a small volume, and an equal volume of 90 per cent. alcohol added. This solution was then evaporated to half its volume and

¹ *Stechr. Chem.* (1868), p. 563.

² *Ber. d. chem. Ges.*, 6, 502.

³ *J. prakt. Chem.* [2], 244.

allowed to stand. On cooling, beautiful, needle-like crystals, nearly an inch long, separated. These were removed and dried, first between filter-paper, then by standing in a desiccator over sulphuric acid. After standing in the desiccator for a day, the crystals began to whiten and crumble, showing that they were losing water of crystallization. The salt was, therefore, recrystallized from 60 per cent. alcohol and dried between filter-paper. In all, about 40 grams of this salt were obtained.

Analysis of the crystallized salt gave the following results: For moisture, 1.1218 grams lost 0.0824 gram at 100° , equivalent to 7.34 per cent. H_2O . $(C_5H_{10}<\overset{OH}{SO_3})_2Ba \cdot 2H_2O$ should contain 7.10 per cent. H_2O .

The salt dried at 100° gave the following figures:

	Calculated for $(C_5H_{10}<\overset{OH}{SO_3})_2Ba$.	Found.
Barium	29.09	29.05
Sulphur	13.58	13.98

Even the last crystals from the mother-liquor gave no test for chlorine, proving that no chlorosulphonic acid was formed.

$(C_5H_{10}<\overset{OH}{SO_3})_2Ba$ and $(SO_3<\overset{OC_5H_{11}}{O})_2Ba$ are isomers. The latter is known to crystallize with $2H_2O$. The former has been reported anhydrous. A concentrated solution of the salt was acidified and boiled with dilute hydrochloric acid. It developed no pink color, no precipitate and no odor of fusel oil. The lead salt was prepared, decomposed by hydrogen sulphide and the free acid boiled. It gave, after long boiling, only a faint test for sulphuric acid. Some isoamyl sulphate was prepared from isoamyl alcohol and concentrated sulphuric acid, and the barium salt formed. The aqueous solution of the latter, even when dilute, when acidified with hydrochloric acid and boiled, gave a pink color, the odor of fusel oil, and a precipitate of barium sulphate. Hence there seemed no doubt that the compound described was barium oxyisoamyl sulphonate, and that it crystallizes with two molecules of water. Mewes¹ has shown that ethyl sulphate, by the action of fuming sulphuric acid, is converted into oxyethyl sulphonic acid. Hence it is possible that the first product of the reaction between isoamyl chloride and fuming sulphuric acid is isoamyl sulphate, and that this, by further action, is converted into the

¹ *Ann. Chem. (Liebig)*, 143, 196.

oxysulphonic acid. There is, however, no experimental evidence to prove this.

CHICAGO VARNISH CO.,
CHICAGO, June, 1903.

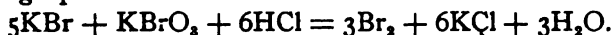
[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 86.]

3,5-BIBROM-2-AMINO BENZOIC ACID: ITS NITRILE AND THE SYNTHESIS OF QUINAZOLINES FROM THE LATTER.¹

BY MARSTON TAYLOR BOGERT AND WILLIAM FLOWERS HAND.

Received July 25, 1903.

ATTEMPTS to brominate nitrites have usually resulted unsuccessfully, and the bromination of anthranilic acid has given only tribromaniline. By the use of the calculated amount of nascent bromine, however, we have succeeded in introducing two atoms of bromine, not only into the molecule of anthranilic acid, but also into that of its nitrile, the brominating agent being an aqueous solution of potassium bromide and bromate, in the proportion of five molecules of the former to one of the latter, which, upon acidifying, liberates exactly 3 molecules of bromine, according to the following equation:



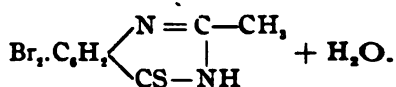
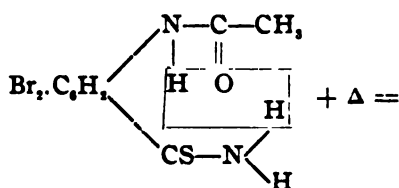
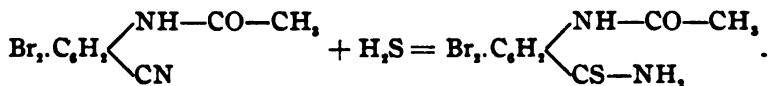
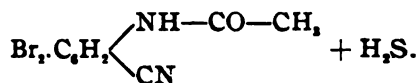
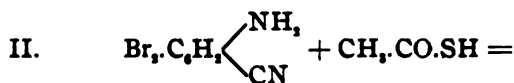
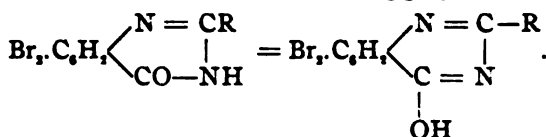
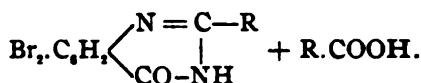
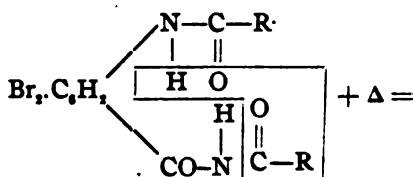
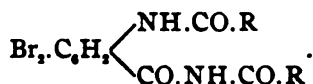
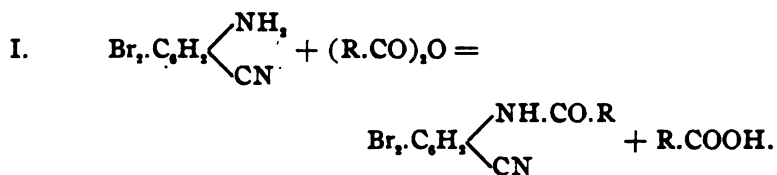
A standard solution of bromide and bromate, 1 cc. of which, upon being acidified, liberated 0.0800 gram of bromine, gave very satisfactory results.

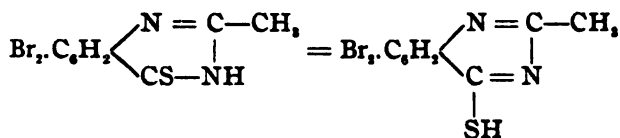
With both anthranilic acid and its nitrile, the bromine entered in the ortho-para positions with reference to the amino group, giving 3,5-bibrom-2-aminobenzoic acid and its nitrile, from which, by elimination of the amino group, 3,5-bibrombenzoic acid and its nitrile were obtained. This elimination of the amino group was accomplished with the greatest difficulty, the yield of the bibrombenzoic compound being small.

The bibromanthranilic nitrile we have converted into quinazolines and thioquinazolines by the use of the methods previously reported by us,² the equations being as follows:

¹ Read at the Cleveland meeting of the American Chemical Society, June 30, 1903.

² This Journal, 24, 1031; 25, 372.





By these reactions, 6,8-bibrom-2-alkyl-4-ketodihydroquinazolines, the corresponding methyl thioquinazoline, and certain of their derivatives have been prepared.

EXPERIMENTAL PART.

BROMINATION OF ANTHRANILIC NITRILE. 3,5-BIBROM-2-AMINO-BENZONITRILE.

The anthranilic nitrile used in these experiments was prepared by the method described in our previous paper.¹

Bromination in Carbon Tetrachloride, Benzene, or Aqueous Solution.—On adding a carbon tetrachloride solution of bromine to a similar one of anthranilic nitrile, a white, amorphous precipitate immediately separates, which melts at (roughly) about 195°-200°. By a single crystallization of this product from alcohol, colorless needles of considerable length are obtained, melting quite sharply at 95.5° (corr.). Bromination in benzene or in aqueous solutions appears to yield similar results. This product has not as yet been further investigated.

Bromination with Hypobromite, and with Nascent Bromine.—Three grams of anthranilic nitrile were dissolved in dilute alcohol, dilute hydrochloric acid added, and then sufficient alkaline potassium hypobromite solution gradually stirred in to form a bibrom-derivative. Small, white, feathery needles separated, which melted sharply at 156°-156.5° (corr.) after several recrystallizations from 95 per cent. alcohol. A portion was sublimed, and the sublimate showed exactly the same melting-point.

	Found.	Calculated for C ₇ H ₄ N ₂ Br ₂ .
Nitrogen	10.38	10.15
Bromine	57.73	58.00

A solution of bromide and bromate of potassium was prepared as already described. The anthranilic nitrile was dissolved in about ten parts of strong alcohol, acidified with hydrochloric acid,

¹ This Journal, 24, 1035.

and the calculated amount of the brominating solution poured in. At first we used a large excess of dilute hydrochloric acid and cooled with ice, but later found both these precautions unnecessary. The brownish substitution product separates at once. It is washed thoroughly, dissolved in the smallest possible amount of 95 per cent. alcohol on the water-bath, hot water added until the cloud formed redissolves but slowly, and the solution is then allowed to cool. The bibromanthranilic nitrile separates very completely, in needles, the yield being nearly theoretical, and the product quite pure. A single recrystallization will usually remove the last traces of color from the crystals, the substance being identical in all respects with that obtained by the action of the hypobromite.

This bibrom nitrile forms no salt when hydrochloric acid gas is passed through its dry ethereal solution; nor is it acetylated by long boiling with acetic anhydride, the amino group remaining unaffected. To determine the position of the bromine atoms in the molecule, the saponification of the nitrile was undertaken.

SAPONIFICATION OF 3,5-BIBROM-2-AMINOBENZONITRILE.

Potassium Hydroxide.—The bibrom nitrile was boiled for some time with caustic potash of various strengths, with but little effect. A small amount was dissolved, and a few white needles separated on cooling. Very strong alkali appeared not to dissolve it at all, while fusion with potassium hydroxide gave only a yellow decomposition product.

Hydrochloric Acid.—The nitrile was unchanged by several hours' boiling with concentrated hydrochloric acid. When they were heated together in sealed tubes at 180° for several hours, partial saponification was secured, accompanied by some decomposition.

Sulphuric Acid.—Concentrated sulphuric acid charred the nitrile, but dissolved it completely on gentle warming. Acid of 75 per cent. to 85 per cent. strength gave a fairly good saponification, but the product was always brown, even after solution in caustic soda and reprecipitation with hydrochloric acid. In a sealed tube at 180° , however, 80 per cent. sulphuric acid gave a satisfactory saponification. Above 185° , rapid decomposition sets in. It is advisable to use as short a sealed tube as possible and to turn the same in the furnace from time to time, as the nitrile sublimes out of the sulphuric acid into the upper end of the tube and is thus liable to escape complete saponification. The contents

of the tube are poured into water, and the precipitate filtered out, washed and crystallized from alcohol, when white needles are obtained melting at 235.5° - 236° (corr.). A portion sublimed showed exactly the same melting-point.

3,5-BIBROM-2-AMINO BENZOIC ACID.

The melting-point of the acid obtained by us, by saponification of the bibromanthranilic nitrile, does not coincide with that of any of the bibromanthranilic acids so far reported.

Hübner¹ gives the melting-point of the 3,5-bibrom-2-amino-benzoic acid as 225° , and exactly the same figure (225°) for the melting-point of the 3,4-bibrom-2-aminobenzoic acid, while Dorsch² found the melting-point of the 3,4-bibrom acid to be 226° - 228° , and states that his acid is identical with that of Smith.³

We, therefore, decided to attempt the bromination of anthranilic acid itself in the same manner as its nitrile, in the hope of obtaining the same bibromanthranilic acid, and in this we were quite successful.

The anthranilic acid was dissolved in a very large volume of dilute hydrochloric acid and the bromide-bromate solution stirred in. The mixture turns blue and a precipitate slowly separates. After standing for half an hour, the precipitate is filtered out, washed thoroughly to remove unchanged anthranilic acid, etc., and then separated from any tribromaniline by solution in cold, dilute caustic soda and reprecipitation with hydrochloric acid.

By using rather less than the calculated amount of the brominating solution, very little tribromaniline is formed; any excess of bromine, however, above 2 molecules, increases the yield of tribromaniline and correspondingly diminishes that of the bibromanthranilic acid. With 3 molecules of bromine to 1 of anthranilic acid, only a trace of the bibromanthranilic acid was found, the product being nearly pure tribromaniline.

The precipitated bibromanthranilic acid is washed and treated with boneblack. The light amber solution thus obtained, on cooling, separates small needles nearly white. These needles are suspended in boiling water, baryta water is added to alkaline reaction, and the excess of baryta then removed by saturating the boiling solution with carbon dioxide. The barium carbonate and

¹ *Ann. Chem. (Liebig)*, 222, 175.

² *J. prakt. Chem. (2)*, 23, 36.

³ *Ber. d. chem. Ges.*, 10, 1706.

a small amount of material insoluble in baryta water are filtered out, and the filtrate evaporated to crystals. On cooling, the barium salt of the bibromanthranilic acid separates in small, white prisms, which are recrystallized from water, and then decomposed by hydrochloric acid. The bibrom acid thus liberated is crystallized from benzene and from alcohol, then appearing in needles of a faint yellowish cast, melting at 235° - 235.5° (corr.), and identical in other respects with the acid obtained by the saponification of the bibromanthranilic nitrile. Both the acid and its barium salt are rather troublesome to purify, their solutions rapidly darkening when heated, and this may account for the low melting-point reported by Hübner.¹ Well-formed crystals can be obtained only by very slow cooling.

The pure 3,5-bibrom-2-aminobenzoic acid, as thus prepared, is easily soluble in alcohol (absolute), ether or acetone; moderately, in 95 per cent. alcohol, boiling benzene, or boiling toluene, but only sparingly in the latter two when cold; insoluble in ligroin; almost insoluble in water, cold or hot. It is decomposed, with loss of bromine, when gently heated with slaked lime. Heated alone in a sealed tube, at 260° - 270° it decomposes with liberation of hydrobromic acid. By elimination of its amino-group, 3,5-bibrombenzoic acid is formed. By the action of dry hydrochloric acid gas upon its dry ethereal solution, the hydrochloride separates as a white powder, which, when washed with dry ether and dried, gives off hydrochloric acid very rapidly.

SALTS OF 3,5-BIBROM-2-AMINOBENZOIC ACID.

Alkaline Salts.—By evaporating concentrated aqueous solutions of the sodium or potassium salts over sulphuric acid *in vacuo*, these salts separate in needles of considerable length. On account of their great solubility in both water and alcohol, it is very difficult to purify them.

Barium Salt.—The preparation of this salt we have already outlined. It crystallizes in small needles, moderately soluble in boiling water, but only sparingly soluble in cold. The crystals carry 3.5 molecules of water, of which 1.5 molecules are removed by drying over sulphuric acid *in vacuo*. According to Hübner¹ the crystals contain $4\text{H}_2\text{O}$.

Some of the crystals, dried five hours at 100° , lost 7.89 per

¹ *Loc. cit.*

cent. in weight; $(C_6H_2Br_2(NH_2)COO)_2Ba.3\frac{1}{2}H_2O$ contains 7.99 per cent. water. A determination of the water in the crystals dried over sulphuric acid, *in vacuo*, gave 4.78 per cent. and 5.05 per cent.; $(C_6H_2Br_2(NH_2)COO)_2Ba.2H_2O$ contains 4.73 per cent. H_2O .

This latter product, containing $2H_2O$, was further analyzed for barium and nitrogen, with the following results:

	Found.		Calculated for $(C_6H_2Br_2(NH_2)COO)_2Ba.2H_2O$.
Barium	17.76	17.83	18.00
Nitrogen		4.90	4.74

When heated in an open tube, this barium salt takes fire and burns. By careful manipulation, however, a sublimate was obtained, melting at $74^\circ-75^\circ$ (corr.), which has not been further examined.

ELIMINATION OF THE AMINO-GROUP FROM 3,5-BIBROM-2-AMINO-BENZONITRILE.

The bibrom nitrile was suspended in water, hydrochloric acid added, and potassium nitrite solution gradually dripped in. No diazotizing whatever occurred, the nitrile being recovered unchanged.

The nitrile was then dissolved in 95 per cent. alcohol, and oxides of nitrogen (from nitric acid and arsenious oxide) passed through the boiling solution. On concentrating the alcohol solution, groups of small needles separated which were dried and carefully sublimed, the sublimate melting sharply at $96.5^\circ-97^\circ$ (corr.). The yield is very small, and subliming at $98^\circ-100^\circ$ in a gentle current of air is the only method by which we have been able to get a product with a sharp melting-point.

The action of ethyl nitrite upon the nitrile was puzzling and unsatisfactory. A boiling 15 per cent. solution of the nitrite was used in large excess, with a few drops of hydrochloric acid. The solution was evaporated to dryness on the water-bath, and the residue crystallized from dilute alcohol, but no pure product could be obtained. On subliming the crude crystals on the water-bath in a gentle current of air, beautiful, white needles were obtained, the melting-point of which rose steadily with the progress of the sublimation. One crop melted at $59^\circ-59.5^\circ$ (corr.), another at $67.5^\circ-68^\circ$ (corr.), and a third at $87^\circ-88^\circ$ (corr.). Saponification of the last lot gave an acid, melting poorly at about 205° , and presumably impure 3,5-bibrombenzoic acid.

The yield in all these reactions was so small that not enough material was secured for an analysis. Conversion of the products, however, to 3,5-bibrombenzoic acid points clearly to the presence of its nitrile. The action of nitrous vapors upon the amino nitrile always gives the same product, melting sharply at 96.5° - 97° (corr.), though in small yield, and we are of the opinion that this is the pure 3,5-bibrombenzonitrile, although Claus and Weil¹ report its uncorrected melting-point as 89° .

Some of this product, melting at 96.5° - 97° (corr.), was saponified by heating it in a sealed tube for three hours at 170° with 75 per cent. sulphuric acid. Like its amino derivative, the bibrom nitrile tends to sublime out of the sulphuric acid and thus escape complete saponification. A short, sealed tube should, therefore, be used, as suggested. From the sealed tube, on cooling, large, glassy crystals separated which were contaminated with unsaponified nitrile. The crude bibrom acid was purified by solution in dilute caustic alkali and reprecipitation with hydrochloric acid. Crystallized from alcohol, the bibrombenzoic acid was obtained in small, glassy needles, softening slightly at 215° and melting at 218.5° (corr.). The crystals sublime quite easily. If the first crude acid is very dark in color, it may, with advantage, be recrystallized from concentrated sulphuric acid, in which it dissolves on warming and separates out unchanged on cooling.

ELIMINATION OF THE AMINO GROUP FROM 3,5-BIBROM-2-AMINO-BENZOIC ACID.

The bibromanthranilic acid was dissolved in absolute alcohol, the solution heated to boiling, and saturated with nitrous gases (from nitric acid and arsenious oxide), causing the solution to assume a deep reddish brown color. The boiling solution was poured into twice its volume of water, and the light yellow precipitate filtered out and thoroughly washed with water. The crude acid thus obtained was converted into its difficultly soluble barium salt, which was purified by repeated crystallizations from water and then decomposed with hydrochloric acid. The purified bibrombenzoic acid was crystallized from benzene, and separated in radiating masses of long, white needles (m. p. 219.5° - 220.5° (corr.)), similar in all its properties to the acid obtained by saponification of the bibrombenzonitrile, and evidently the 3,5-bibrombenzoic acid. The complete purification of this acid is very tedi-

¹ *Ann. Chem.* (Liebig), 269, 223.

ous, small amounts of impurities lowering the melting-point considerably.

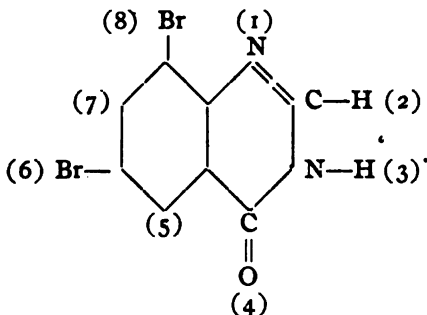
Barium Salt of 3,5-Bibrombenzoic Acid.—This was prepared by the action of baryta water upon the purified acid. It can be purified by crystallization from water, in which it is less soluble than the barium salt of the bibrom amino acid. It separates in needles of a faint yellow color. The air-dried salt was analyzed with the following results:

	Found.	Calculated for (C ₇ H ₃ Br ₂ O ₂) ₂ Ba. 3 $\frac{1}{2}$ H ₂ O.
Water	8.58	8.31
Barium	18.03	18.07

Angerstein¹ gives the melting-point of 3,5-bibrombenzoic acid as 223°-227°; Hübner,² as 213°-214°; Claus and Weil,³ as 209° (uncorr.). Hübner and Claus and Weil assign to the Ba salt 4 molecules H₂O; Angerstein dried the salt over H₂SO₄ and then found 2H₂O.

SYNTHESIS OF QUINAZOLINES FROM 3,5-BIBROM-2-AMINO BENZO-NITRILE.

6,8-Bibrom-4-Ketodihydroquinazoline,



Three grams bibromanthranilic nitrile were heated in a sealed tube with 3 cc. glacial formic acid for five hours at 225°-235°. This temperature was much higher than necessary, as the tube was under heavy pressure when opened and the contents were black. By solution in dilute caustic soda and saturation of the alkaline liquid with carbon dioxide, a yellow precipitate separated in small amount.

¹ *Ann. Chem.* (Liebig), 188, 10.

² *Ibid.*, 222, 171.

³ *Ibid.*, 269, 224.

A second tube, containing 3 grams of the nitrile and 3.5 cc. glacial formic acid, was heated for sixty-nine consecutive hours at 200°-209°, and the contents worked up in the same manner. A beautiful, white crystalline substance was obtained which, after recrystallization from aniline, formed small, clear needles. The yield of pure substance was about 50 per cent. of the theoretical. It does not melt, but decomposes above 300°. On analysis, the substance gave 9 per cent. nitrogen, while the above formula requires 9.21 per cent. nitrogen.

Ethyl Ether of 6,8-Bibrom-4-Ketodihydroquinazoline.—One-half gram of the quinazoline was heated for two and a half hours in a sealed tube with slight excess of alcoholic sodium hydroxide and excess of ethyl iodide, at 100°-104°. The beautiful, crystalline product was washed with water and with alcohol, and then formed a snow-white mass of small, clear needles, melting sharply at 229°-230° (corr.). On analysis, 8.70 per cent. nitrogen was found; required for $C_{10}H_8ON_2Br_2$, 8.43 per cent.

6,8-Bibrom-2-Methyl-4-Ketodihydroquinazoline.—Two grams of the nitrile and 2 cc. of acetic anhydride were heated together for about six hours in a sealed tube at 220°-230°. By solution of the tube's contents in dilute caustic soda, filtering and saturating the filtrate with carbon dioxide, a snow-white product was obtained, which was recrystallized from aniline. By very careful heating, in a current of carbon dioxide, it may be partly sublimed in beautiful needles. It does not melt, but decomposes slowly when heated above 300°. It shows about the same solubilities as the methyl thioquinazoline (see beyond), except that it is rather more soluble in glacial acetic acid.

	Found.	Calculated for $C_{10}H_8ON_2Br_2$.
Nitrogen	9.14	8.81
Bromine	50.03	50.31

We have run a number of sealed tubes for the preparation of this quinazoline, varying the temperature and the duration of the heating, but in every case so far the yield has been very poor.

Ethyl Ether of 6,8-Bibrom-2-Methyl-4-Ketodihydroquinazoline.—One-half gram of the quinazoline was heated for two and a half hours at 100°-105° in a sealed tube with slight excess of alcoholic sodium hydroxide and excess of ethyl iodide. No crystals separated on cooling. The alcoholic solution was evaporated to a small

volume; the brown needles which crystallized out were recrystallized from alcohol, but still retained a slight brownish color. They began to decompose very slowly at about 170°, but did not melt at 290°.

6,8-Bibrom-2-Ethyl-4-Ketodihydroquinazoline.—Three grams nitrile and 3 cc. propionic anhydride were heated together in a sealed tube for ten and a half hours at 200°, followed by five hours longer at 210°. On treating the tube's contents with sodium hydroxide and carbon dioxide, as already described, the ethyl quinazoline was obtained as a white precipitate. Crystallized from moderately dilute alcohol, it separates in long, white, silky needles (m. p. 278°-280° (corr.)). The yield was poor.

0.2148 gram substance gave 8.10 per cent. nitrogen; required, 8.43 per cent.

6,8-Bibrom-2-Normalpropyl-4-Ketodihydroquinazoline.—Three grams nitrile and 3 cc. normal butyric anhydride were heated together in a sealed tube for ten and a half hours at 200°, followed by five hours and a half at 210°. Treatment of the tube's contents in the usual manner resulted in the separation of the N-propyl-quinazoline as a white, voluminous precipitate. It crystallizes from dilute alcohol in colorless, microscopic needles (m. p. 238°-240° (corr.)). The yield is only fair.

0.2351 gram substance gave 8.07 per cent. nitrogen; required, 8.09 per cent.

6,8-Bibrom-2-Isopropyl-4-Ketodihydroquinazoline.—Three grams of the nitrile and 3 cc. of isobutyric anhydride were heated together in a sealed tube for ten and a half hours at 200°, followed by five and a half hours at 210°, and then two hours longer at 220°. The tube's contents were worked up as the others were. The isopropyl quinazoline thus produced appears to the unaided eye as a white, amorphous powder, but is really a felted mass of white, microscopic, hairy crystals, which melt at 259°-260° (corr.). The yield was only fair.

0.2228 gram substance gave 7.92 per cent. nitrogen; required, 8.09 per cent.

6,8-Bibrom-2-Isobutyl-4-Ketodihydroquinazoline.—Three grams of the nitrile and 3 cc. of isovaleric anhydride were heated together in a sealed tube for ten and a half hours at 200°, five and a half hours at 210°, and two hours at 215°-220°. The tube's contents were

worked up in the usual manner, and the isobutyl quinazoline separated as a precipitate. The recrystallized substance forms colorless, microscopic needles (m.p. 230° - 231.5° (corr.)). 0.1999 gram substance gave 7.82 per cent. nitrogen; required, 7.77 per cent.

Most of these brominated quinazolines decompose wholly or partly on melting. It is interesting to note that with increase in molecular weight the melting-point steadily sinks, iso compounds showing a higher melting-point than those with normal side-chains. We have already called attention to the same condition of affairs in the case of the unbrominated alkyl quinazolines and the acylated anthranilic nitriles.

These brominated quinazolines dissolve very readily in caustic alkali, but do not appear to form salts with the mineral acids.

6,8-Bibrom-2-Methyl-4-Thioetodihydroquinazoline.—Two grams of the bibromanthranilic nitrile and the calculated amount of thiacetic acid were heated together in a sealed tube for about six hours at 220° - 230° . On opening the tube, slight pressure, due to hydrogen sulphide, was observed. The contents of the tube were boiled with dilute alkali, the solution cooled, filtered, and carbon dioxide passed through the filtrate, whereby a yellow, amorphous precipitate separated. Crystallized from aniline, this precipitate changed to beautiful, yellow needles. The substance does not melt at 290° , but decomposes slowly when heated. By very careful heating in a gentle current of carbon dioxide, it may be partially sublimed. It is nearly insoluble in alcohol, benzene or 50 per cent. acetic acid, slightly soluble in glacial acetic acid, and soluble in boiling aniline. It is only moderately soluble in caustic alkalies; when enough alkali is used to dissolve the quinazoline completely and a few drops of acetic acid are then added, the quinazoline is partly reprecipitated, although the solution remains strongly alkaline to litmus.

The temperature used in the first experiment (220° - 230°) was unnecessarily high, as partial decomposition had occurred, and the yield of thioquinazoline was poor. Another tube, heated sixty-nine hours at 200° - 209° , likewise showed too much decomposition. A third tube, heated forty-two hours at 180° , was much more satisfactory in appearance; but little decomposition had occurred, and a yield of 2.1 grams of the pure thioquinazoline was obtained from 3 grams of the bibromnitrile.

Analysis of 6,8-Bibrom-2-Methyl-4-Thioketodihydroquinazoline.

—The determination of carbon and hydrogen in this bibrom-thioquinazoline proved exceedingly troublesome, on account of the high percentage of bromine (nearly 48 per cent.) and the presence of sulphur.

The de Roode mixture of red lead and lead chromate was used as the oxidizing agent, and it was found to be much more efficient with freshly prepared lead chromate than with the commercial fused article. Freshly precipitated and thoroughly washed lead chromate was mixed with red lead and made into little balls. These were dried, ignited in an open dish, and then thoroughly burned out in a stream of dry oxygen. As thus prepared, they did not melt or disintegrate.

A long combustion tube was used, in which were placed an oxidized copper gauze, then a long porcelain boat containing the thioquinazoline mixed with ignited red lead and covered with the same, then a short, silver spiral, followed by the oxidizing mixture, a long, silver spiral, and a bright copper gauze. The combustion was conducted very slowly at a moderate temperature. Unless the temperature of the exit end of the tube was kept well down, bromine could be detected in the gases passing into the absorption train.

	Found.	Calculated for $C_9H_6N_2SBr_2$.
Carbon	32.94–32.76	32.33
Hydrogen	2.01–2.03	1.80
Nitrogen	8.70–8.52	8.38
Sulphur	9.64	9.58
Bromine	47.79	47.91

Ethyl Ether of 6,8-Bibrom-2-Methyl-4-Thioketodihydroquinazoline.—This was prepared by the method already described for the corresponding oxygen compound. The product crystallized out of the sealed tube on cooling. Washed with water and with alcohol, it appeared in beautiful, light yellow needles, which began to decompose at about 305° , but did not melt completely at 360° .

[CONTRIBUTION FROM THE LABORATORY OF THE LOUISIANA AGRICULTURAL
EXPERIMENT STATION.]

A CONTRIBUTION TO THE CHEMISTRY OF RICE OIL.

By C. A. BROWNE, JR.

Received January 2, 1900.

I. THE CHEMICAL AND PHYSICAL CONTENTS OF RICE OIL.

BUT very little attention has been paid thus far to the chemistry of rice oil, notwithstanding the very extensive use of rice as a food product. The only data, which the writer has been able to find, is a report by Smetham¹ upon an oil obtained from Rangoon rice-meal by hydraulic pressure, the meal containing about 15 per cent. oil. The oil, as thus expressed, had a dirty green color, and was partly solid at the ordinary temperature. It appeared to be especially remarkable for the large proportion of free fatty acids present, the percentage of which ranged from 31.6 to 77.2. A saponification value of 193.2 and an iodine absorption of 96.4 were also reported.

In connection with some investigations recently carried out at the Louisiana Experiment Station in New Orleans, upon rice and the various by-products of the rice-milling industry, some attention was paid to rice oil. A number of oil samples were examined, including the oil extracted from the rice itself, as well as that obtained from the bran or meal. The latter comprises the gluten layer and germ of the rice grain and, when unadulterated with hulls, contains nearly 15 per cent. oil.²

The chemical and physical constants of an oil obtained from a sample of rice bran are given in the following table:

TABLE I.—CONSTANTS OF RICE OIL.

Specific gravity $\frac{99^\circ}{99^\circ}$	0.8907
Melting-point (point of liquefaction)	24°
Acid number	166.2
Saponification number	193.5
Ether number	27.3
Iodine number	91.65
Reichert-Meissl number	1.1
Mean molecular weight of insoluble fatty acids	289.3
Melting-point of insoluble fatty acids	36°

The above oil was semisolid in consistency during the winter ;

¹ *J. Soc. Chem. Ind.* (1893). p. 848.

² Calculating the rice-meal to a water-free and starch-free basis, there would be about 20 per cent. oil in the pure gluten and germ.

it began to melt at about 24° , but did not become perfectly transparent until 47° . During the warm summer, the oil liquified partly and consisted then of a brownish-colored oil with a deposit of crystallized fats. The high acid number is noteworthy, corresponding to 83.5 per cent. of free oleic acid. In this respect the oil shares the peculiarity of those analyzed by Smetham. The fact that rice oil contains fats of high melting-point and fatty acids of high mean molecular weight would indicate the probable presence of such higher homologues as arachidic, behenic or lignoceric acids. This supposition was strengthened by the granular deposit of insoluble soaps which settled out after saponifying the oil with alcoholic potash. Further researches as to the constitution of rice oil are greatly to be desired.

II. THE CAUSES PRODUCING ACIDITY IN RICE OIL.

In studying the feeding value of different rice products, our attention was called to the fact that animals frequently showed a marked distaste to rice bran or meal as a food. An inquiry into the cause of this showed that in such cases the feed was very rancid and that this rancidity was due to the very acid condition of the rice oil. Experiments made upon fresh rice bran showed that the oil from the same was only slightly acid, but that upon standing any great length of time a rapid development of acidity took place in the oil, the feed at the same time becoming rancid. In large bulks the development of rancidity in rice-meal seems to be accompanied by a heating and caking of the material.

Instances of such excessive acidity as those noted for rice oil, have been observed in the case of a few other vegetable oils. Palm oil is especially characterized by a high content of free acid. Lewkowitsch¹ states that "even in the fresh state the proportion of fatty acids in palm oil, calculated as palmitic acid, amounts to 12 per cent., and may in older samples reach as much as 100 per cent.—in other words, the splitting-up of the glycerides may become complete." Olive kernel oil² and olive oil³ expressed from the marc also contain large quantities of free fatty acids.

It has long been a recognized fact that atmospheric oxygen, especially in the presence of light, is a very important factor in the decomposition of oils and fats. This influence would no doubt

¹ Lewkowitsch : "Analysis of Oils, Fats, and Waxes," 2nd edition, p. 517.

² Benedikt : "Analyse der Fette und Wacharten," 3. Aufl., p. 458.

³ *Ibid.*, p. 447; see also Lewkowitsch : *Loc. cit.*, p. 451.

be greater with oil in a finely divided condition, as would be the case in rice meal. There is, however, another explanation possible for the decomposition of rice oil besides that of oxidation. The work of different investigators shows that in many cases a decomposition of vegetable oil is produced by means of a fat-splitting enzyme—*lipase*. Reynolds Green¹ has reported the presence of lipase in the germinating seeds of the castor oil plant and Sigmund² has demonstrated its existence in both the resting and germinating seeds of rape, poppy, hemp, flax and maize. The crushed seeds of these plants produced in all cases a development of acidity in neutral emulsions of oil. That the hydrolysis of the oil was due to an enzyme, was shown by the fact that control experiments, in which the enzymes had been killed by boiling, developed no acidity. The high degree of acidity in palm oil and olive-marc oil has also been attributed to enzyme action.³

LIPASE IN RICE BRAN.

An aqueous extract of rice bran was prepared by allowing 20 grams of the material to soak in 100 cc. of cold water for several hours. 25 cc. of the clear filtered extract, when mixed with 5 cc. of commercial hydrogen peroxide, produced a rapid evolution of oxygen, the quantity of this exceeding 100 cc. within a few minutes. The bran extract also produced with tincture of guaiac a strong blue coloration, after adding a few drops of hydrogen peroxide. Both of the above reactions failed with bran extract which had been boiled. Many plant juices and extracts cause a catalytic decomposition of hydrogen peroxide, and give the blue reaction with guaiac and the peroxide; these properties have been thought by some investigators to belong to nearly all enzymes, though Loew⁴ considers them characteristic of two special ferments, *catalase* and *peroxidase*. Without entering into a discussion of this question, we may say that the above reactions, while showing that enzymes are present in rice, do not throw much light upon their specific nature or functions.

To determine whether or not a lipatic ferment is present in rice bran, use was made of the well-known emulsion test. Twenty

¹ Reynolds Green : "Soluble Ferments and Fermentation," p. 227.

² Sigmund : "Ueber fettspaltende Fermente im Pflanzenreiche," *Monatsh. Chem.* (Vienna), 11, 272 (1890).

³ Lewkowitsch : "Notes on Fat-Splitting Enzymes," *J. Soc. Chem. Ind.* (1903), p. 69.

⁴ Loew : "Catalase, a New Enzyme of General Occurrence," Report No. 68, U. S. Dept. of Agr.; see also Report No. 65 by same author, "Physiological Studies of Conn. Leaf Tobacco," pp. 30-34.

cc. of the clear bran extract were thoroughly shaken up with an equal volume of a thick emulsion of castor oil, and the mixture rendered faintly alkaline to litmus solution. After standing at the laboratory temperature for twenty-four hours, the solution began to turn pink, and in two days had become a deep red. A similar experiment, conducted with extract which had been previously boiled, remained alkaline; likewise, blanks of the unboiled extract to which no emulsion had been added, so that the development of acid could only come from the action upon the oil of a fat-splitting enzyme. To prevent the formation of acid products by bacteria, 0.25 per cent. of potassium cyanide was used in each experiment as a germicide. The cyanide may have exerted an inhibitive effect upon the activity of the enzyme, yet the necessity of using an antiseptic agent in such tests is imperative, as was shown by the fact that, when no cyanide was employed, neutral solutions of bran extract became acid to litmus in a few hours. After standing a week, the acid emulsion in the above experiment was shaken out with ether, and the ethereal solution filtered and evaporated to dryness. The oil thus obtained had an acid number of 29.7, which would indicate that about 16 per cent. of the oil had undergone hydrolysis.

To determine the hydrolyzing effect of lipase upon rice oil under natural conditions, the following experiment was conducted. A sample of fresh rice bran was taken to the laboratory immediately after milling and divided into two portions. One portion was subjected to a dry heat of 90° C to destroy any enzymes; the other portion remained untreated. Both samples were tied up in sacks and set aside for one month. The acidity of the oil from the fresh bran (containing 14.3 per cent. oil) was determined, and also that of the oil obtained from the raw rice used in manufacturing the bran. The same determinations were also made on the oils extracted from the two samples of bran after standing one month. The results of the work are given in the following table:

TABLE II.

Source of oil.	Acid number.	Free acid as oleic. Per cent.
Raw rice	13.8	6.9
Fresh bran (six hours after milling).....	24.7	12.5
Bran, one month old, unheated	123.8	62.2
" " " " heated.....	47.0	24.0

The above results show that an exceedingly rapid decomposi-

tion of the oil in the unheated bran had taken place. In the oil of the bran, which had been heated, there was also some development of free acid, but the quantity formed was less than one-fourth that developed in the oil of the unheated sample. The experiment would indicate that while the development of acidity in rice oil may be, to a slight extent, the result of oxidation, it is to a much greater degree the effect of a fat-splitting enzyme.¹

The sample of raw rice, from which the bran used in the experiment was made, was taken from a large quantity that had been lying in storage in a New Orleans warehouse many months. The oil from the bran six hours after milling, compared with the oil from the original rice, shows an increase in free acid of 5.6 per cent. This shows that a rapid decomposition of the rice oil sets in immediately after milling, the activity of the enzyme² seeming thus to depend upon an exposure of the oil-bearing tissues of the rice grain to the air. The amount of free acid in the oil within the rice grain is probably less than that indicated in Table II, as some decomposition no doubt took place during the grinding of the grain, before the extraction with ether.

The foregoing experiments have a certain practical interest, since a destruction of the lipase at once suggests itself as a means for the prevention of rancidity in rice-meal and similar products. By subjecting the material, directly after milling, to a dry heat sufficient to destroy the enzyme, such as is done in the kiln-drying of certain feeds, the development of rancidity would be largely checked.

III. THE DIGESTIBILITY OF RICE OIL.

In connection with some feeding experiments, recently conducted at this Experiment Station, with rice bran and rice polish, the following coefficients of digestibility for rice oil were obtained. Two steers were used in the work.

	Rice bran. Per cent. oil digested.	Rice polish. Per cent. oil digested.
Steer No. 1.....	52.0	66.0
" " 2.....	57.5	81.2
Average	54.8	73.6

There are several facts which may explain the greater digesti-

¹ For further particulars as to the action of lipase, see the work of Kastle and Loevenhart (*Amer. Chem. J.*, 24, 491 (1900)).

² The enzyme is probably the product of an antecedent substance or *zymogen*, this transformation not taking place except when the seed is crushed or while it is germinating. (See Reynolds Green, "Soluble Ferments and Fermentation," p. 381.)

bility of the rice oil in the polish. In the experiment with rice polish, the steers received only about one-third the quantity of oil given in the bran experiment and may thus have been able to digest a greater percentage of oil from the ration. The bran was very coarse, containing about 30 per cent. of rice hulls; the polish was free from hulls, and contained more of the starchy part of the rice than the bran. The oil from the bran contained 83.5 per cent. free fatty acids, the oil from the polish 47.5 per cent. The conditions may, therefore, have been more favorable in the polish towards securing a more complete digestion of the oil. Individuality of the animal is seen to play an important part. Steer No. 2 digested a greater percentage of oil in both experiments, the difference in the case of the polish being especially marked.

In the bran experiment, the oil from the feed and the undigested oil from the feces were analyzed. A comparison of the two sets of constants shows very noticeable differences, and throws some light upon the changes which the rice oil undergoes during digestion.

TABLE III.—SHOWING EFFECT OF DIGESTION UPON COMPOSITION OF RICE OIL.

Constant.	Oil from rice bran.	Oil from feces of steers fed on rice bran.
Melting-point (point of liquefaction)...	24°	58°
Acid number	166.2	144.2
Saponification number	193.5	176.0
Ether number	27.3	31.8
Iodine number.....	91.65	27.08
Mean molecular weight insoluble fatty acids.....	289.3	320.2
Melting-point insoluble fatty acids.....	36°	60°

The oil obtained from the feces was light-colored and of wax-like consistency. The soaps obtained on saponifying this oil with alcoholic potash were marked by a low degree of solubility in alcohol. The oil extracted from the feces was no doubt contaminated to some extent with metabolic products from the animal, such as biliary substances and fatty bodies from the intestines. Some unsaponifiable matter was present, but this was removed before determining the constants of the fatty acids. Beef-fat from the intestines, according to Mayer,¹ has the following constants:

¹ Wagner's *Jahresberichte* (1880), 644.

Melting-point	50°
Saponification number	196.2
Melting-point insoluble fatty acids	47.5°
Mean molecular weight insoluble fatty acids	278.2

The presence of fat, sluffed off from the walls of the intestinal tract, could not, therefore, explain the differences noted in Table III. The most satisfactory and plausible explanation of the facts is a difference in digestibility of the various constituents of the rice oil. The liquid unsaturated bodies are very largely absorbed in the process of digestion, as is shown by the marked decrease in the iodine number. The fatty acids of lowest molecular weight are also the easiest to assimilate; hence, the oil excreted in the feces consists largely of a residue of acids of high mean molecular weight and high melting-point. Reference was made, in the first section of this paper, to the probable presence in rice oil of such higher acids as arachidic, behenic, or lignoceric, and this supposition finds support in the character of the fatty acids in the oil from the feces, these having a mean molecular weight higher even than the molecular weight of arachidic acid (312).

Stearic acid, the highest saturated fatty acid in the animal body, has a molecular weight of 284, and saturated fatty acids of greater molecular weight than stearic are probably assimilated by the animal only to a limited extent.

In conclusion, the writer desires to express his indebtedness to Dr. W. C. Stubbs, under whose direction the work was carried on, for advice and encouragement.

[CONTRIBUTION FROM BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, NO. 50. SENT BY H. W. WILEY.]

OLIVE OILS AND OLIVE OIL SUBSTITUTES.

BY L. M. TOLMAN AND L. S. MUNSON.

Received July 13, 1903.

SOURCES OF THE OILS.

IN AN investigation of olive oils and their substitutes, a number of pure California and Italian olive oils were obtained and analyses of them made. The California oils were largely obtained from representative producers, with affidavits as to their purity. The Italian oils were received through agents in Italy. The collection of oils thus made contained samples from most of the oil-producing districts of both countries.

The varieties of olives used are given, to a certain extent, with California oils, but with the Italian oils it was impossible to obtain this information. The methods of analysis used were those given in the U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin 65, pp. 20-35.

FATTY ACIDS.

By liquid fatty acids are meant the acids, the lead soaps of which are insoluble in ether, and by the solid fatty acids, those the lead soaps of which are insoluble in ether. This method of separation, while not absolutely exact, gives a very close approximation of the amounts of saturated or solid fatty acids and unsaturated¹ or liquid fatty acids. The iodine number of the liquid fatty acids was determined exactly as with the Hübl method on oils. Great care is necessary in drying the liquid fatty acids to prevent oxidation and in this work they were dried at about 70° C., in a current of coal gas.

TABLES OF ANALYSES.

In Table I are the analyses of thirty-eight samples of California olive oil and eighteen samples of Italian olive oil. These are mostly virgin or first-pressing oils, but a few oils have been included which cannot be classed as edible oils. These are not included in the average or maximum and minimum, but are given in order to show what widely varying results may be obtained with pure oils, and that the cause of these abnormal results would not be detected unless the determination of free acids was made. The amount of free acids present in an oil affects the specific gravity and index of refraction to a marked degree. Sample No. 22,619, with an index of refraction of 1.4672 and 44.40 per cent. of free acid, and No 673 with specific gravity of 0.9149 and 12.11 per cent. of free acids are examples of this fact. It seems very probable that some of the very low figures on these determinations, reported by various analysts, would be explained if the free acid had been determined.

DISCUSSION OF ANALYTICAL DATA.

An examination of Table I will show that on the high-grade oils there is only a very small variation in specific gravity and index of refraction for both the California and Italian oils. The wide range in Maumené figures means nothing, as different strengths of acid were used, but the specific temperature figures

TABLE I, PART I—PURE CALIFORNIA OLIVE OILS.

Serial No.	Variety and locality.	Specific gravity at 15.5° C.	Butyro-refractometer reading at 15.5° C.	Index of refraction at 15.5° C.	Maxwell number.	Specific temperature reaction.	Hbl number.	Iodine number of liquid fatty acids.	Saponification number.	Melting-point of fatty acids, °C.	Solid fatty acids, Per cent.	Free fatty acids as oleic, Per cent.
23,692	Mission olive, Chico	0.9168	68.5	1.4713	85.6	96.6	191.2	22.6	5.12	0.95
23,463	" " Concord	0.9164	68.4	1.4712	48.0	106.6	85.6	91.5	191.9	21.3	4.92	0.79
22,713	" " Santa Barbara	68.7	1.4715	85.3	94.9	191.1	22.4	5.11	0.73
22,714	" " " 1	68.5	1.4713	84.6	...	191.5	22.4	3.87	1.26
22,715	" " " 2	68.2	1.4711	84.7	...	191.3	20.5	2.02	2.73
23,458	" " " "	0.9169	68.7	1.4715	48.4	107.5	88.2	94.9	191.4	23.5	4.42	0.73
838	" " San Diego	0.9169	69.2	1.4718	49.5	108.5	86.2	...	190.6	24.0	6.15	1.07
839	" " " "	0.9171	69.2	1.4718	48.4	106.0	89.0	...	189.9	21.2	4.94	3.51
840	" " " "	0.9169	68.9	1.4716	48.2	105.7	86.3	...	189.4	24.0	5.94	1.09
23,457	" " Santa Clara	0.9166	68.3	1.4711	47.0	104.4	86.2	91.2	191.6	21.1	3.39	0.97
832	" " " "	0.9173	68.8	1.4715	47.6	100.1	84.9	...	189.3	20.5	5.40	0.85
834	" " " "	0.9168	68.8	1.4715	46.2	97.2	84.5	...	189.3	19.4	6.03	0.34
23,505	" " Santa Barbara	0.9171	68.5	1.4713	47.1	104.2	88.5	94.5	191.5	20.2	2.43	1.54
798	" " " "	0.9177	68.8	1.4715	51.0	107.3	89.7	...	190.0	19.2	...	0.63
795	" " " "	0.9177	69.0	1.4717	50.0	105.2	89.7	...	189.8	19.8	4.73	0.75
796	" " " "	0.9177	68.8	1.4715	52.1	103.7	89.8	...	189.9	19.2	4.69	0.61
797	" " " "	0.9177	68.8	1.4715	50.2	105.6	89.8	...	189.7	19.6	5.44	0.63
22,617	Redding picholine olive, Berkeley ¹	67.3	1.4706	78.5	...	194.4	30.2	...	0.36
23,462	picholine olive, Oroville	0.9162	66.9	1.4703	43.0	95.5	79.9	91.7	192.2	31.0	10.91	0.79

² Common grade of oil for lubricating.¹ Made in 1893.¹ Second pressing.

TABLE I, PART I (Continued)—PURE CALIFORNIA OLIVE OILS.

Bertal No.	Variety and locality.	Specific gravity at 15.5° C.	Butyro-refractometer reading at 15.5° C.	Index of refraction at 15.5° C.	Measure number.	Specific temperature reaction.	Hbl. number.	Iodine number of liquid fatty acids.	Saponification number.	Melting-point of fatty acids, °C.	Solid fatty acids, Percent.	Free fatty acids as oleic, Percent.
23,461	Picholine olive, Guérneville.....	0.9162	67.5	1.4707	45.0	100.0	83.0	92.4	192.0	28.0	7.62	1.07
22,619	Manzanillo olive, Berkeley ¹ ,	62.0 ²	1.4672	79.6	...	191.8	24.5	...	41.40
23,456	Italian varieties olive, Santa Clara	0.9169	68.3	1.4711	47.7	106.0	84.3	93.4	191.9	23.4	7.23	0.53
831	" " " "	0.9168	68.8	1.4715	46.6	98.1	85.2	...	189.3	20.6	...	0.61
833	" " " "	0.9170	68.8	1.4715	48.0	101.0	84.8	...	189.8	20.2	6.55	0.65
506	Mixed varieties olive, Los Angeles	0.9174	68.5	1.4713	38.0	98.9	84.4	...	193.1	22.4	...	0.71
836	" " " "	0.9174	68.8	1.4715	48.2	105.7	86.0	...	190.7	24.8	...	2.51
837	" " " "	0.9167	68.4	1.4713	45.0	98.6	84.2	...	190.3	23.6	5.16	0.51
835	" " " "	0.9167	68.2	1.4711	44.8	98.2	82.7	...	190.4	26.0	6.19	0.96
21,091	" " Cloverdale	0.9167	68.8	1.4715	45.3	94.5	81.9	...	190.0	26.6	12.96	1.42
3,460	" " Yolo	0.9167	68.2	1.4711	47.0	104.0	85.7	93.8	190.4	23.4	6.24	2.24
22,618	Mixed olives, Berkeley ³	67.5	1.4707	83.7	...	192.5	20.7	...	8.21
23,124	" " Redlands	0.9171	68.2	1.4711	45.5	...	83.7	92.5	193.3	25.4	6.20	0.47
841	" " " "	0.9168	68.8	1.4715	47.1	98.3	86.9	...	189.4	21.6	8.61	0.20
842	" " " "	0.9168	68.7	1.4715	46.8	97.7	87.2	...	189.5	21.4	7.52	0.21
843	" " " "	0.9169	68.6	1.4714	45.6	95.2	85.1	...	189.6	22.8	4.33	0.28
23,459	" " Napa	0.9162	67.7	1.4709	45.5	101.2	82.9	90.3	191.6	25.0	5.69	1.72
673	" " " "	0.9149 ²	66.4	1.4699	45.5	95.0	83.3	...	189.5	21.6	7.58	12.11
23,649	" " Oroville	0.9164	68.0	1.4710	43.5	96.6	83.4	88.9	192.1	22.6	...	1.43

1 Poor quality.

Second pressing.

³ Not included in the average on account of high percentage free acid.

TABLE I, PART II.—PURE ITALIAN OLIVE OILS.

Serial No.	Locality.	Specific gravity at 15.0° C.	Butyro-refraction meter reading at 15.0° C.	Index of refraction at 15.0° C.	Refractive number.	Specific temperature reaction.	Häbl number.	Iodine number of liquid fatty acids.	Saponification value.	Melting-point of fatty acids, °C.	Solid fatty acids. Per cent.	Free fatty acids as oleic. Per cent.
580	Bari	0.9177	67.9	1.4709	39.6	103.1	81.8	...	191.7	28.5
933	Puglia.....	0.9158	67.7	1.4708	43.5	95.6	80.4	94.8	192.0	26.2	16.47	1.02
960	Bari	0.9159	67.6	1.4707	41.7	101.8	80.9	96.0	191.4	26.6	16.37	0.80
961	Bitonti	0.9162	67.6	1.4707	43.5	95.6	80.8	96.5	191.7	27.3	13.67	0.69
935	Puglia.....	0.9162	67.7	1.4708	44.2	97.1	80.5	95.1	191.9	29.3	15.20	1.03
936	"	0.9155	67.7	1.4708	44.8	98.4	81.8	96.2	191.5	26.2	11.07	2.79
962	Bari	0.9159	67.6	1.4707	43.5	99.1	81.2	96.5	191.8	27.9	17.72	0.62
931	Toscana	0.9166	67.6	1.4707	44.4	97.4	80.7	89.8	189.6	25.8	5.01	0.82
932	Lucca	0.9167	67.5	1.4707	44.4	97.4	80.5	...	190.1	25.2	8.07	0.80
958	"	0.9158	68.0	1.4710	48.0	102.3	81.8	90.6	190.4	22.9	6.04	0.79
959	"	0.9164	68.0	1.4710	46.2	98.4	81.5	92.0	190.5	23.9	7.95	0.53
934	Genoa	0.9159	67.6	1.4707	42.5	96.8	81.1	92.4	190.6	24.5	8.60	0.62
952	Liguria	0.9160	68.0	1.4710	45.0	97.9	81.4	90.5	190.1	21.6	7.38	0.61
953	"	0.9161	67.3	1.4705	47.0	100.0	79.2	90.8	191.3	24.9	9.76	1.18
954	"	0.9180	68.5	1.4713	48.3	103.0	86.1	97.5	190.5	25.0	7.76	2.55
955	"	0.9157	67.8	1.4709	44.2	97.1	82.6	94.8	190.8	23.5	8.93	1.09
957	"	0.9166	68.0	1.4710	45.0	97.9	82.1	91.1	189.7	21.6	5.53	1.90
956	Abruzzi	0.9164	68.3	1.4712	49.1	104.7	84.5	98.4	190.7	28.5	13.51	0.37
	"	0.9168	68.2	1.4711	46.8	101.6	85.1	92.8	190.6	22.5	...	0.85
	California oils											
	{ Average ..	0.9180	69.2	1.4718	52.1	109.7	89.8	92.6	194.6	31.0	12.96	3.51
	{ Maximum ..	0.9162	66.9	1.4703	38.0	94.5	78.5	88.9	189.3	19.2	2.02	0.20
	{ Minimum ..	0.9163	67.8	1.4709	44.9	99.1	81.5	94.0	...	25.4	...	1.11
	Italian oils...											
	{ Average ..	0.9180	68.5	1.4713	49.1	104.7	86.1	98.4	192.0	29.3	17.72	2.79
	{ Maximum ..	0.9155	67.3	1.4703	39.6	95.6	79.2	89.8	189.6	21.6	5.01	0.57
	{ Minimum ..											

1 First grade.

2 Second grade.

do not show such a wide variation. The average for California oils is a little higher, due probably to the higher iodine value of the oils examined. The reason for including the figures given by the Maumené test is that the specific temperature figures are affected to a certain degree by the strength of the acid, as was shown by the work of Sherman, Danziger and Kohnstamm.¹ This will account for the somewhat lower specific temperature numbers obtained by De Negri and Fabris,² and Milliau, Bertainchand and Malet³ on French and Algerian oils, as they used an acid which gives a rise of temperature with water of about 36° to 37° C., while the acid used in this work gives a rise of from 45° to 46° C.

The variation found in the Hübl numbers of the oils is very wide and the same is true with the iodine figures on the liquid fatty acids. The variation in the Hübl figures is, to a considerable extent, controlled by the amount of solid fatty acids present, but is also affected by the composition of the liquid fatty acids, as the wide variation in the iodine absorption of these acids shows. The Italian oils are not very different from the California oils in this particular, and this work is confirmed by De Negri and Fabris⁴ in their recent extensive work on Italian oils.

These results make it evident that the iodine absorption alone can have little value in determining the purity of an oil, as all but very gross adulteration can be covered up by this range of from 78.5 to 89.8 for the Hübl figures. The average for the Hübl figures on the oils examined is higher for the California oils than for Italian oils, but from all the figures available on pure oils there is not so wide a difference. De Negri and Fabris⁴ found an average of 83.7. In fifty-seven samples of commercial Italian olive oil, imported into this country, in which no adulteration was detected, the average figure was 80.5.

The melting-point of the fatty acids—the point where the acids in a capillary tube became clear—also showed wide variation and a very close relation to the percentage of solid fatty acids, as would be expected. These oils were all tested qualitatively for cottonseed, peanut and other seed oils, with negative results in all cases.

¹ This Journal, 24, 266.

² "Ann. Lab. chim. Cent. delle Gab.," Vol. I, Gli Olii, Part I.

³ "Rap. sur les Huiles D'Olive de Tunisie," 1900.

⁴ Loc. cit.

TABLE II.

Ref. No.	Kind of oil.	Specific gravity at 15.5° C.	Butyro-refraction at 15.5° C.	Index of refraction at 15.5° C.	Mass number.	Specific temperature reaction.	Hbl number.	Iodine number of liquid fatty acids.	Saponification value.	Melting-point of fatty acids, °C.	Solid fatty acids, Per cent.	Free fatty acids as oleic, Per cent.
773	Cocunut	0.9259	49.1	1.4587	21.0	44.0	8.58	31.9	259.5	25.2	65.9	0.11
494	Palm	0.9128	53.0	99.0	201.0	49.2	...	19.53
22,433	Lard	0.9148	67.4	1.4706	47.8	106.2	75.9	94.0	195.7	33.2	18.90	0.75
23,606	"	0.9160	69.5	1.4720	46.5	103.3	69.7	95.8	197.7	38.4	26.68	0.28
499	Peanut ¹	0.9186	70.0	1.4723	46.5	129.1	87.8	...	191.8	34.3	...	0.40
772	"	0.9188	71.3	1.4431	63.2	135.3	96.3	114.6	189.9	36.4	...	0.24
495	Mustard. Black mustard	0.9170	76.5	1.4762	68.2	189.4	103.8	...	176.0	21.5	4.05	0.38
770	Brown "	0.9184	76.2	1.4760	77.6	165.4	110.4	114.2	178.5	20.6	1.06	0.48
771	Black "	0.9193	76.5	1.4762	79.4	169.3	113.0	119.8	182.8	20.8	2.32	0.34
776	Yellow "	0.9147	74.5	1.4750	61.4	130.9	98.4	103.1	173.0	21.0	tr	0.13
496	Rape	0.9143	74.3	1.4749	54.9	152.5	92.7	101.5	174.7	21.9	1.02	0.63
775	"	0.9163	74.1	1.4748	63.6	135.6	101.3	105.1	176.6	20.5	tr	1.26
1,187	Almond	0.9186	70.9	1.4728	45.3	117.6	96.2	...	192.5	23.2	...	0.48
23,624	Sunflower	0.9201	72.7	1.4739	108.3	113.8	192.3	21.0	3.67	0.18
498	"	0.9205	72.1	1.4736	60.0	166.7	104.1	...	191.2	21.0	4.12	1.72
777	Maize	0.9253	77.5	1.4768	89.2	190.2	123.3	134.5	189.9	21.6	7.44	3.65
1,186	Cottonseed	0.9236	75.6	1.4757	67.1	174.3	110.9	...	198.5	38.0	...	2.17
1,159	" "butter oil"	0.9226	72.5	1.4738	66.4	172.9	103.8	143.0 ^a	197.1	35.5	22.90	0.07
1,160	" "summer white"	0.9226	72.3	1.4737	73.4	191.1	106.2	145.4 ^a	196.9	39.0	22.43	0.07
1,161	" "cooking oil"	0.9226	72.8	1.4737	66.2	172.4	104.8	145.7 ^a	196.0	39.6	23.60	0.04
774	Poppy	0.9244	77.8	1.4770	75.8	213.0	134.9	142.0	193.8	25.8	6.67	0.90
1,188	Linseed	0.9318	88.8	1.4831	179.5	...	191.7	19.2	3.88	0.40

¹ 3.78 per cent. arachidic acid, melting-point, 72.5° C.² 4.12 per cent. arachidic acid, melting-point, 72.0° C.^a Iodine value calculated.

Table II contains the results of analysis of a number of pure oils of various kinds, some of which were pressed in the laboratory and others were pressed under our supervision. The lard oils were obtained from Armour & Co., and cottonseed oils, except No. 1,186, from the American Cotton Oil Company. The lard oil No. 23,606 was a pure white product and free from lardy odor, except when heated. The peanut oils were cold-pressed from American nuts. The cocoanut oil was from fresh cocoanuts.

The mustard, rape and poppy oils were prepared from seeds which were identified by Miss Charles, of the Seed Laboratory of the U. S. Dept. of Agriculture, as follows:

770	Brown mustard	<i>Brassica Arvensis</i> (Charlock).
771	Black "	<i>Brassica Juncea</i> (Indian mustard).
776	Yellow "	<i>Sinapis Alba</i> (yellow mustard).
775	Rape seed	<i>Brassica Napus</i> .
774	Poppy seed	<i>Papaver somnifer</i> (opium poppy).

The other oils were prepared from commercial seeds or nuts and were cold-pressed. These oils, with the exception of linseed, are used as substitutes or adulterants of olive oil and were analyzed in order to obtain more complete data on American oils, there being very few published results on oils of this class.

The Maumené test was made on the oils having a high iodine number by using a weaker acid, as suggested by Sherman, Danziger and Kohnstamm.¹

The relation between the solid fatty acids, the Hübl number and the iodine number of the liquid fatty acids should be noted. The mustard oils have a higher Hübl number than cottonseed-oil, but having only a small percentage of solid fatty acids, the true iodine number, as it is sometimes called, is only a little higher than the Hübl number, while the cottonseed-oils, with a large percentage of solid fatty acids, have a much higher iodine figure for the liquid fatty acids.

The relation of the iodine number of the liquid fatty acids to the drying properties of the oil is shown to the greatest extent in cottonseed and poppy oils. The iodine numbers of the liquid fatty acids of the two oils are practically the same and their drying properties are practically the same, but the Hübl number of poppy oil is 134.9 and cottonseed-oil 103-105. In this case, the Hübl number gives very little idea as to the drying capacity of the oil. This same relation holds true with other oils. Rape oils and cottonseed-

¹ This Journal, 24, 266.

oil with the same Hübl number have very different powers of absorbing oxygen.

The true iodine figure gives a much better idea of the nature of the unsaturated fatty acids present than the Hübl figure. Sample No. 23,606, with a Hübl number of 69.7, but containing 26.68 per cent. of solid fatty acids, has an iodine number of the liquid fatty acids of 95.8, which is practically the same as that given by olive oils, showing that the liquid portion of lard oil is very similar to the liquid portion of olive oil.

The Hübl figure depends largely on the method of making the oil, whether hot- or cold-pressed. The unsaturated fatty acids of the cocoanut oil are very different from those of the palm oil, the former having an iodine figure of 31 and the latter, of 99. This figure closely agrees with that of oleic acid, the unsaturated acid of lard and olive oils.

The iodine number of liquid fatty acids can be calculated from the iodine number of the oil and the per cent. of solid fatty acids, if one assumes that the total fatty acids in an oil is 95.5 per cent.

The total fatty acids less the solid fatty acids give the liquid fatty acids. From the following formula, the iodine number of the liquid fatty acids can be calculated:

$$A = \frac{I \ 100}{L}$$

A = Iodine number liquid fatty acids.

I = Hübl number.

L = Percentage liquid fatty acids.

The peanut oils Nos. 499 and 772 show quite a difference in iodine number, but it can be seen that a very large amount of either of these oils could be mixed with olive oil without changing any of the physical or chemical properties enough to certainly show its presence.

The only reliable test is the separation of the arachidic acid. These two samples had 3.78 and 4.12 per cent. of this acid present, which melted at from 72° to 72.5° C.

In all of these oils, even those taken fresh from the press, free fatty acids were found, showing that they must have existed as such in the seeds. The three samples of commercial cottonseed-oil contained only traces of free acid due to the process of refining, while sample No. 1,186, which had not been refined, but was fresh from the press, contained 2.17 per cent.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, LABORATORY OF INSECTICIDES AND AGRICULTURAL WATERS, U. S. DEPARTMENT OF AGRICULTURE. NO. 51. SENT BY H. W. WILEY.]

A MODIFICATION OF THE AVERY-BEANS METHOD FOR DETERMINING TOTAL ARSENIOUS OXIDE IN PARIS GREEN.

BY J. K. HAYWOOD.

Received June 26, 1903.

INTRODUCTION.

UNTIL recently, nearly all methods for determining total arsenious oxide in Paris green, in so far as the author has been able to find by careful search of chemical literature, were based upon the oxidation of all arsenic to the "ic" condition and a subsequent precipitation with magnesia mixture, followed by a gravimetric determination as magnesium pyroarsenate. Some oxidized with hydrochloric acid and potassium chlorate and determined the arsenic in the presence of copper; some oxidized with fuming nitric acid and determined the arsenic in the presence of copper, and others first removed the copper by boiling with sodium hydroxide and oxidized the filtrate with hydrochloric acid and potassium chlorate, but all finally precipitated the arsenic with magnesia mixture and weighed as magnesium pyroarsenate.

While a few chemists determined the arsenic by precipitation along with copper as the sulphide and a subsequent separation of the two sulphides, this method, on account of inherent difficulties, was seldom employed.

During 1899 Smith¹ devised a volumetric method based on a titration of the arsenious oxide in Paris green after all of the copper had been removed and the arsenic reduced to the "ous" condition. This method was a great improvement over the old ones in that one could make a determination of the total arsenious oxide in a single sample of Paris green in about forty-five minutes.

During September, 1900, the author² published a paper upon "The Adulteration and Analysis of Arsenical Insecticides" in which a comparison was made of the Smith method and two or three of the old methods mentioned above. It was shown by this study that the old methods based on the magnesium precipitation

¹ This Journal, 21, 769.

² *Ibid.*, 22, 568.

gave low results, while the Smith method always gave correct results, if a few simple precautions were taken that had not been mentioned by Smith in his original article.

In 1901, Avery and Beans¹ published a method for determining total arsenious oxide in Paris green. Since this method is the one that is to be critically studied, it will be given in full.

Method.—Sample the Paris green (as one would an ore for assaying) down to about 1 gram. Pulverize this small sample in an agate mortar and weigh out 0.2 to 0.3 gram in a beaker of, say, 300 cc. capacity. Add 25 cc. of water, and to the green suspended in the water add, with constant stirring, concentrated hydrochloric acid till solution is just effected. Six to twelve drops are usually sufficient. Now add to the acid solution sodium carbonate solution till a slight permanent precipitate is formed. Dissolve this precipitate by adding 2 to 3 grams of sodium potassium tartrate in solution. Now dilute to about 200 cc., add solid sodium bicarbonate and starch solution, and titrate with iodine in the usual way.

In a critical study that was made of this method in comparison with others, by the Association of Official Agricultural Chemists, it was shown by the author and other chemists that most excellent results were obtained when pure samples of Paris green were examined, but that when samples of greens containing considerable quantities of free arsenious oxide were examined, the method always gave low results. This was due to the fact that the free arsenious oxide was not dissolved by hydrochloric acid in the cold. Since any method that is to be used for determining total arsenious oxide in Paris green should include the free arsenious oxide, which is one of the most common adulterants, it at once became evident that the method would have to be modified to admit of its application in general work, especially in station control work. As this method, with pure Paris greens, is accurate as well as extremely short (only about five minutes being required for a single determination), it appeared to the author that any slight modification of it which would allow of its application to Paris greens containing free arsenious oxide, would be well worthy of some study. With this end in view, the following experimental work was carried out.

EXPERIMENTAL WORK.

Experiment 1.—It was at first thought the method might be modified in the following manner: Carry the manipulation down

¹ This Journal, 23.

to the point where hydrochloric acid has been added, a drop at a time, to get the Paris green in solution. At this point all Paris green will be dissolved, while most of the free arsenious oxide will remain undissolved. Now add a slight excess of sodium carbonate and boil to get all arsenious oxide into solution, cool, acidify with hydrochloric acid, a drop at a time, add sodium bicarbonate until a faint precipitate is apparent, then sodium potassium tartrate, then an excess of sodium bicarbonate and after dilution titrate with iodine in the ordinary way.

Working in this way upon a Paris green that had been shown to contain 67.98 per cent. total arsenious oxide by the Smith method, of which 27.50 per cent. was free arsenious oxide, the following results were obtained: 66.55 per cent.; 67.50 per cent.; 67.15 per cent.; and 67.70 per cent. It at once became evident that, while this method sometimes gave practically correct results, the tendency was toward low results, so that it was not to be depended upon unless the factors that caused the variation could be discovered and controlled.

Since prolonged boiling of *arsenious* compounds with alkalis is apt to cause the formation of *arsenic* compounds, it was thought that the length of time of boiling the solution might cause the reduction in the amount of arsenious oxide found. To test this, definite weights of the Paris green were treated as above, using 1 gram of sodium carbonate for each determination, and the boiling was continued for varying lengths of time. The following results were obtained:

Time of boiling. Minutes.	Arsenious oxide. Per cent.
4	67.26
8	67.26
10	63.95
20	63.43
30	Decided reduction of the copper.

It appeared then, from the above table, that the longer the boiling was continued the lower the results, and that the low results were caused by the action of sodium carbonate on the Paris green, resulting in the reduction of the copper and consequent oxidation of part of the arsenious oxide.

Since only slightly low results were obtained when the green was boiled for from four to eight minutes with 1 gram of sodium carbonate, it was thought that by reducing the amount of the

sodium carbonate and only boiling from four to eight minutes, the error due to the action of the sodium carbonate upon the Paris green might be so reduced as to be negligible. Working upon this basis, the following results were obtained :

Time of boiling. Minutes.	Amount of sodium carbonate used in excess of that necessary to neutralize the hydrochloric acid.	Arsenious oxide found. Per cent.
7	7 drops of a saturated sodium carbonate solution.	67.39
7	4 drops of a saturated sodium carbonate solution.	67.44

Even in this case, with a minimum of sodium carbonate and a minimum time of boiling, low results were obtained and it was evident that the method was worthless.

Experiment 2.—An attempt was made to use sodium bicarbonate instead of sodium carbonate; the method in all its other details was the same as described in Experiment 1.

Working in this way upon the same Paris green, the following results were obtained where definite weights of the green were used; a definite quantity of sodium bicarbonate (10 grams) was added in each determination and the time of boiling was varied.

Time of boiling. Minutes.	Arsenious oxide. Per cent.
5	67.44 (a few flakes of arsenious oxide undissolved.)
10	67.96
10	67.96
15	67.35
20	66.92
40	63.43 (decided reduction of copper.)

It appeared from the above table that five minutes' boiling was not sufficient to cause all of the free arsenious oxide to go into solution; that ten minutes' boiling gave theoretical results, while with fifteen, twenty and forty minutes' boiling the results were progressively lower, until at forty minutes a marked reduction of the copper and consequent oxidation of arsenious oxide were shown.

The ten-minute period of boiling with 10 grams of sodium bicarbonate was tried with various other Paris greens, but low results were obtained in so many cases that it was seen that the time of boiling must be altered for different samples, thus rendering the method valueless.

An attempt was made to reduce the amount of sodium bicarbonate and so get correct results, but it was found that unless the sodium bicarbonate was present in comparatively large quantities, the free arsenious oxide went into solution very slowly, so that a prolonged boiling was necessary, which always resulted in a slight reduction of the copper of the Paris green.

Experiment 3.—The only other way of applying the Avery-Beans method of analysis to Paris green containing free arsenious oxide that suggested itself to the author was to separate the undissolved, free arsenious oxide and the dissolved arsenious oxide and to determine them separately. To do this the following method of analysis was used: Sample the Paris green (as one would an ore for assaying) down to about 2 grams. Pulverize this small sample in a mortar and place from 0.3 to 0.4 gram in a beaker. Add about 25 cc. of water and, while constantly stirring, add concentrated hydrochloric acid, a drop at a time until all the Paris green is in solution and the free arsenious oxide remains as a residue. Filter and wash the residue. The arsenious oxide in the filtrate is determined in exactly the same manner as is given in the original Avery-Beans method. The filter and contents are dropped back into the beaker, which also receives the water used in washing the funnel. Five grams of sodium bicarbonate are added and the solution boiled until the arsenious oxide is completely dissolved (this takes from five to ten minutes). The resulting solution is cooled and acidified, using a drop of methyl orange to read the change. It is then made alkaline again with sodium bicarbonate, starch is added and the arsenious oxide titrated in the usual way with standard iodine. By this method the results given in the following table were obtained. There are also given the results obtained by the Smith method, which we know to be correct, and a determination of the free arsenious oxide by the sodium acetate extraction method and by the ten-day water extraction method.

Sample No.		Soluble As_2O_3 sodium acetate extraction.	Soluble As_2O_3 10-day water extraction.	Total As_2O_3 Smith method.	Total As_2O_3 modified Avery-Beans method.
1...		7.25	8.75	58.98	59.17
"	2...	13.50	14.90	61.71	61.68
"	3...	26.00	28.00	67.60	67.42
"	4...	7.18	8.19	59.86	59.87

It will thus be seen that by modifying the Avery-Beans method

as above, it can be applied to Paris green containing free arsenious oxide and will give results which are strictly comparable with the Smith method. While this modification increases the time of carrying out the analysis on a single sample from about five to twenty minutes, it still results in a method which is much shorter than any known by the author for this class of compounds.

Now that the above modification has been worked out, it appears so simple and obvious that the author almost feels reluctant to publish it. When it is taken into consideration, however, that the Avery-Beans method has been before the Association of Official Agricultural Chemists for two years and that, although its limitations were spoken of, no one suggested the above change; that the author has also worked with the method for about two years without previously thinking of the change and that finally Avery and Beans, the originators of the method, did not suggest the above simple modification so that it might be applied to Paris green adulterated with arsenious oxide, it seems that the results are worthy of publication, especially since a shorter time and fewer manipulations are involved than in any other method for determining arsenious oxides in Paris green at present known to the author.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 87.]

A MODIFICATION OF THE BABCOCK-BLASDALE VISCOSITY TEST FOR OLIVE OIL.

By HERBERT ABRAHAM.

Received June 26, 1903.

ACCORDING to Blasdale, Prof. Rising was the first to suggest the possibility of using the factor representing the viscosity of the soap solution formed from a fixed amount of olive oil, saponified by a definite amount of potassium hydroxide, for detecting adulterated samples. At his suggestion Babcock, who had in 1886¹ examined a number of samples of butter and its principal adulterants, tested also a few of the most common fatty oils. His results show that butter gave the soap of lowest viscosity, and he also remarked that among the fatty oils, olive gave one of about the highest viscosity. The method was, at this time, used simply

¹ Reports N. Y. State Agricultural Experiment Station, 1886, p. 338; and 1887, p. 380.

for the examination of butter, and it was only in 1895 that Blasdale¹ applied it to olive oils. His paper contains the results obtained from a number of samples of pure and commercial olive oils, and also from a few oils which might be used as adulterants of olive oil. The figures obtained with different pure samples of olive oil varied considerably, but were always higher than those of the adulterated oils.

The method was considered especially promising for the detection of lard oil and as, at present, no good method is known by which the presence of the latter in olive oil can be determined with any degree of accuracy, its importance is obvious.

That this method has not come into more general use may be ascribed to the difficulty experienced in obtaining concordant results.

The writer has undertaken to study and, as far as possible, to mitigate or obviate the causes which led to the discrepancies in the method as hitherto carried out.

At first the method used by Blasdale² was strictly followed, but this was soon modified with respect to the means of determining the viscosity of the soap solution eventually obtained. Doolittle's viscosimeter³ was employed in the earlier tests, but the cost of this instrument has restricted its use to but a few laboratories. Moreover, for the present purpose there seems to be no theoretical advantage in measuring the viscosity by the torsion method, and no objection to the use of a viscosimeter which determines the rate of flow of the liquid through an aperture. In addition to being accurate, inexpensive, and easy of manipulation, it is important that the instrument used should be of such construction as to be readily kept at the desired temperature. Ostwald's viscosimeter⁴ appears to meet these requirements more satisfactorily than any other with which the writer is familiar, and it was thought that a comparison of this with the Doolittle viscosimeter might yield results of value. The following were obtained on testing aqueous solutions of sucrose.

¹ This Journal, 17, 937 (1895).

² Fifteen grams of oil are weighed in a saponification flask, and treated with 30 cc. of water containing exactly 7.5 grams potassium hydroxide, and 10 cc. of alcohol. This is heated on a water-bath until complete saponification has been effected. The resulting soap is washed into a large evaporating dish, heated until all the alcohol is expelled, and diluted to exactly 500 cc. at 15° C. The viscosity is determined by means of a torsion viscosimeter and calculated in terms of grams sugar per liter.

³ This Journal, 15, 173 (1893).

⁴ Ostwald-Luther: "Physico-Chemische Messungen," 2nd edition (1893), p. 266.

Grams sugar per liter.	Doolittle's viscosimeter.				Ostwald's viscosimeter.	
	I.		II.		III.	
	Retardation at 26.6° C.	Differ- ences.	Log. decrs. at 20° C.	Differ- ences.	Abs. viscosime- ter at 20° C.	Differ- ences.
0	6.7	..	255	..	100	..
100	7.1	0.4	295	40	132	32
200	7.5	0.4	345	50	186	54
300	8.0	0.5	410	65	306	120
400	8.9	0.9	500	90	455	149
500	11.0	2.1	670	170	712	257
600	14.5	3.5	1448	736
700	21.5	7.0
800	32.8	11.3
900	71.5	38.7

Column I gives the results expressed by the method employed by Doolittle, Column II by the method used by Babcock,¹ and Column III in terms of the absolute viscosity as will be used throughout the following work.

It will be noted that Columns I and III are obtained directly from the readings, while the results in Column II have been increased without rendering them more accurate, by obtaining the logarithmic decrements and then multiplying by 10,000. In spite of this, however, the ranges between the consecutive figures in Column III are greater than those in the other two columns. Ostwald's viscosimeter is, therefore, quite as delicate as Doolittle's. It costs about forty cents, whereas the Doolittle viscosimeter is sold for \$65. Moreover, Ostwald's instrument requires for a test only about one-hundredth as much of the liquid, and, on account of its smaller size, it is easier to maintain at the desired temperature throughout the operation.

The changes which next suggested themselves were (1) the avoidance of transferring the soap from one vessel to another, and (2) the use of a smaller bulk of soap solution.

Both were effected by employing one-fifth the quantities of oil, potassium hydroxide,² and of alcohol used by Blasdale. This corresponds to a soap solution of 100 cc.

As the results of considerable study of the details of manipulation, it was found that the principal causes of variable results obtained by the method are (1) variations in the amount of

¹ Report N. Y. State Agricultural Experiment Station for 1886, p. 316; also *J. Anal. Chem.* (1887), 1, 151.

² This amount was subsequently diminished slightly in order to obtain more concordant results.

caustic potash present in excess; (2) incomplete expulsion of the alcohol used in saponification; (3) absorption of carbon dioxide by the excess of alkali, during the expulsion of the alcohol; (4) varying the temperature at which the actual viscosity is determined; (5) varying the dilution of the soap solution.

Each of these points was studied separately with a view of finding the best conditions of manipulation.

Varying the Amount of Potassium Hydroxide Used.—It was found that the viscosity of the soap solutions increased rapidly with the amount of potassium hydroxide present in excess of that

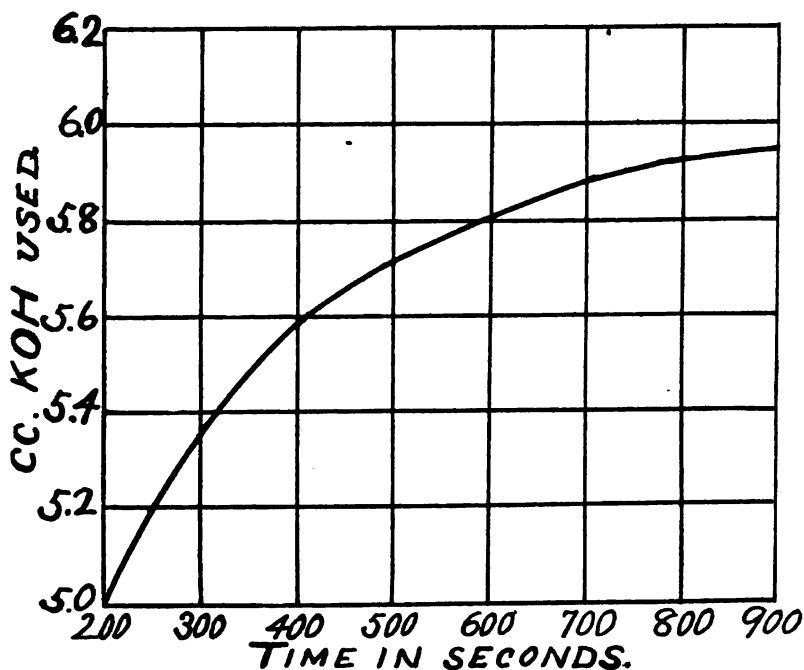


Fig. 1.

required for saponification. Thus, with an olive oil, saponified with 5 cc.¹ potassium hydroxide, the average time of flow was 200 seconds; with 5.2 cc., 253 seconds; with 5.4 cc., 310 seconds; with 5.6 cc., 412 seconds; with 5.8 cc., 568 seconds; with 6 cc., the soap was too viscous to test to any degree of accuracy.

These results are plotted in the form of a curve (Fig. 1). It is evident from these experiments that relatively small variations

¹ One cc. containing $\frac{1}{4}$ gram exactly.

in the amount of free alkali present cause large changes in the viscosity of the solution. Even the variations due to the differences in the Koettstorfer figure of different samples may seriously affect the results. It is much better, therefore, instead of using a *fixed amount* of alkali in each case, to determine the alkali required for the saponification of each sample, and then vary the amount of alkali taken so that the soap solution to be tested will always contain a *fixed excess* of potassium hydroxide.

Expelling the Alcohol Completely with "Ordinary Air."—The same oil saponified with 4.80 cc. potassium hydroxide (2.50 cc. in excess of that required for saponification) etc., and the alcohol expelled completely by a current of air passed over the surface of the liquid, gave an average time of flow of 148 seconds.

Expelling the Alcohol Completely with "Ordinary Air" as above, Followed by Passing in Carbon Dioxide (Converting all the Caustic into Carbonate).—The same oil under this treatment gave an increase of 93 seconds in the time of flow, while the soap solution of another oil, whose original time of flow was 137.2 seconds, was increased by nearly 23.8 seconds.

These and other irregularities led to the conclusion that the use of carbon dioxide is unsatisfactory.

Expelling the Alcohol Completely with Air Free from Carbon Dioxide.—The same oil saponified as above, and having a stream of pure air passed over its surface for half an hour while being heated on a water-bath, gave an average time of flow of 151.6 seconds.

This led to the adoption of air free from carbon dioxide.

Length of Time Required to Expel the Alcohol.—Saponification as above with a Kroonig valve in fifteen minutes, the viscosity being determined directly without expelling the alcohol, gave an average time of flow of 143 seconds.

Another portion saponified in fifteen minutes, with air free from carbon dioxide passed through for fifteen minutes, gave an average time of flow of 150.4 seconds.

A third portion saponified as above, air free from carbon dioxide being passed in for ten minutes, gave an average time of flow of 15.2 seconds.

Ten minutes was, therefore, considered sufficient for the removal of the alcohol.

Varying the Temperature.—Saponified with 4.80 cc. potassium hydroxide, etc., in fifteen minutes, air free from carbon dioxide being then passed in for ten minutes. When the soap solution was tested at 15° C., the time of flow was 205.3 seconds; at 16° C., 196.0 seconds; at 17° C., 185.0 seconds; at 18° C., 172.7 seconds; at 19° C., 161.3 seconds; at 20° C., 150.4 seconds; at 21° C., 142.0 seconds; at 22° C., 134.3 seconds; at 23° C., 127.0 seconds; at 24° C., 120.0 seconds; at 25° C., 114.0 seconds.

The results are plotted in a curve (Fig. 2).

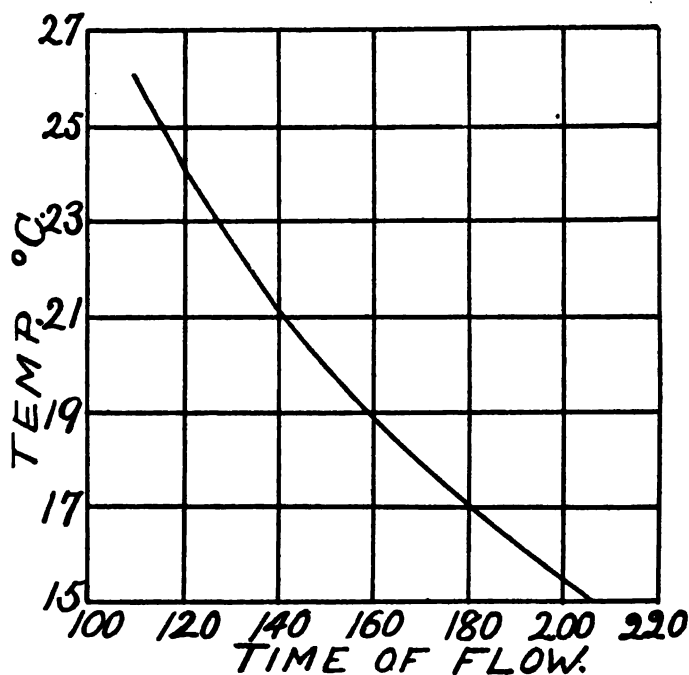


Fig. 2.

Varying the Dilution of the Soap Solution.—The average time of flow of a certain soap solution was 161 seconds; the same, three-quarters strength, was 120 seconds; one-half strength, 105 seconds; one-quarter strength, 98 seconds; for water alone, 95 seconds. The results are plotted in Fig. 3.

In order to avoid or minimize any variations arising from the above conditions, and to obtain a solution of such a viscosity as to permit of convenient and accurate measurement, the following details should be observed:

(1) In every case add exactly 2.5 cc. of potassium hydroxide (0.25 gram per cubic centimeter) in excess of that required for saponification. This amount is desirable as it gives a comparatively low viscosity, offering the following advantages: (a) It takes less time to flow, reducing the total time of the method; (b) the soap dissolves more easily; (c) the results are more uniform and are just as accurate.

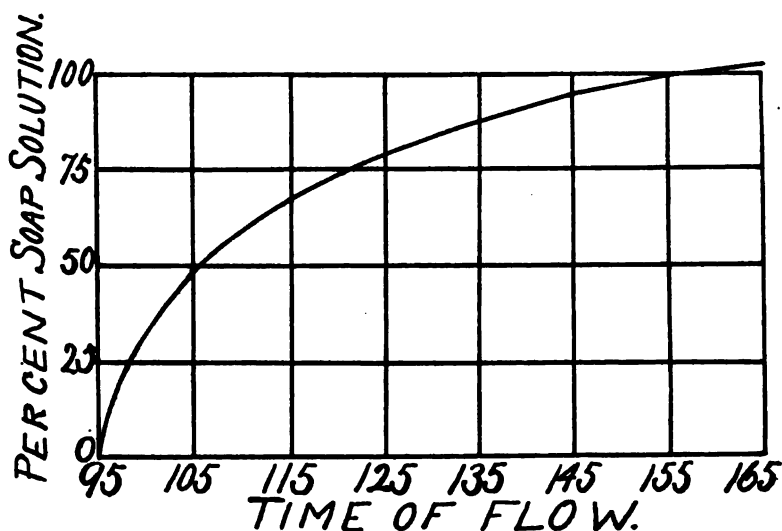


Fig. 3.

(2) Two cc. of alcohol are chosen as being the minimum amount to secure rapid saponification.

(3) The alcohol should be expelled completely by means of a stream of air, free from carbon dioxide, passed through the flask for about ten minutes. This secures the greatest accuracy combined with the greatest rapidity.

(4) The soap should be diluted to 100 cc. in conformity with the above conditions.

(5) The viscosity should be determined at *exactly* 20° C.

THE METHOD AS FINALLY ADOPTED.

I. Apparatus.—(a) 100 cc. flasks accurately calibrated and thoroughly cleansed and dried; (b) a “water-suction apparatus” capable of raising a column of mercury at least 300 mm.; (c) a 5 cc. measuring pipette, graduated accurately to $\frac{1}{20}$ cc. for measuring out the potassium hydroxide solution. The end of this

pipette should be drawn out into a thin-walled capillary so as to decrease the size of the drops and thus render the delivery more accurate. The diameter of the capillary should be such that 60 to 65 drops of the potassium hydroxide solution are delivered per cubic centimeter;¹ (d) a stopper with a Kroonig valve to fit the 100 cc. flasks, used while saponifying. This permits any vapors to escape, but does not allow air to enter the flask, thus avoiding contamination by carbon dioxide; (e) a ring-stand carrying a water-bath and U-tubes to remove carbon dioxide from the air used; (f) an Ostwald viscosimeter and accessories.

II. Reagents—(a) A solution of potassium hydroxide containing *exactly* 0.25 gram per cubic centimeter, made up accurately by titration; (b) alcohol practically free from impurities, used in titrating. This should be tested for acidity and neutralized, if necessary; (c) a solution of phenolphthaleïn, 1 gram per liter in pure alcohol; (d) ether for washing out the viscosimeter, pipettes, etc.; (e) standard hydrochloric acid approximately N/5.

III. Determination.—Weigh out two portions of exactly 3 grams of the oil into 100 cc. flasks, care being taken not to introduce any on the necks of the flasks.

Determination of the Amount of Potassium Hydroxide Required for Saponification.—To one portion add 5 cc. potassium hydroxide and 2 cc. alcohol from their respective pipettes. Adjust the seal and heat on the water-bath for from ten to fifteen minutes, when the saponification should have taken place. Rinse the soap into a beaker with about 100 cc. pure alcohol, add 10 to 12 drops phenolphthaleïn, and titrate with hydrochloric acid. Calculate the amount of potassium hydroxide to be added next time in order that there shall be 2.5 cc. in excess of that required for saponification.

Preparing the Soap Solution.—To the second portion of oil, add the calculated amount of potassium hydroxide, and 2 cc. alcohol. Adjust the seal and saponify on the water-bath. The time required for saponification may be materially reduced by occasionally twirling the contents of the flask. If thus agitated at intervals, it rarely takes longer than ten minutes. After saponification, the seal is replaced by a stopper carrying two tubes, a short one and

¹ The pipette used by the writer was calibrated by weighing the water which it delivered at 20° C.; when 5 cc. were delivered altogether the accuracy was $\pm 1_{100}$ cc., while the greatest error for any individual cubic centimeter was 1_{70} cc.

a long one, drawn out so as to come about 5 to 10 mm. above the surface of the liquid. The lower end of the longer tube is curved upwards so as to present the mechanical carrying off of the liquid. The other end of this tube is connected with the suction, while the shorter tube is connected with the absorption train. By placing the finger over the entrance to the last U-tube, a partial vacuum is created in the flask, and the evaporation of water and alcohol is accelerated, as is seen by the frothing of the soap. The finger is removed, and the operation repeated once or twice at intervals. The evaporation should not be carried so far as to remove the water present, else the soap will solidify and take an inconveniently long time for its subsequent solution. It will suffice to take the soap down to the consistency of molasses (which requires five to ten minutes). Without allowing it to cool, the flask is filled about half full of boiling water. Upon rotating, the soap should go into solution in a minute or two. The flask is now immersed in a stream of cold water until it attains about the temperature of the room, when it is diluted to the mark with cold, distilled water and mixed well by shaking.

Finding the Viscosity.—The viscosimeter should be cleaned by attaching it to suction and running first alcohol and then ether through it; it is then immersed in a cylinder filled with water kept *exactly* at 20° C.

Great care must be exercised on introducing the 3 cc. of soap solution into the viscosimeter, and, on sucking it up the capillary (which must be done very slowly), because if it once becomes frothy, it will be almost impossible to secure a satisfactory reading. With a little practice in manipulation, however, the soap can be maintained free from enclosed bubbles during the entire operation. The first reading is usually rejected so as to give the liquid a chance to assume the temperature of the surrounding water-jacket. Five or more closely agreeing readings should be averaged to obtain the time of flow. The readings should agree within two seconds. The instrument is first calibrated by using pure, distilled water which should take in the neighborhood of 100 seconds to flow through. Since the instruments are made of capillary tubes of different diameters, one should be selected which takes about 100 seconds with water—this being most satisfactory for the method.

The "absolute viscosity" is calculated by means of the following formula:

$$v_1 = \left(\frac{s_1}{t} \right) t_1,$$

where t_1 = the time of flow,

s_1 = the specific gravity of the liquid under consideration.

and t = the time of flow of water under like conditions.

The specific gravities of the soap solutions of all the principal oils, as based on a large number of determinations, were found to approximate 1.07 (within ± 0.005), so that this figure may be substituted in place of s_1 in the above expression. An extreme error of 0.005, due to this assumption, will merely affect v_1 by 0.5 to 0.7.

The formula, therefore, reduces to

$$v_1 = kt_1,$$

where k is a constant for the particular apparatus employed. The value of v_1 for pure, fresh olive oil of good quality is usually 165-185, for most other oils it is about 125-135.

In general, it is advisable to determine the viscosity of the soap solution while fresh, as it has been found that after standing several days the viscosity is sometimes increased and sometimes decreased.

In the hands of the writer, the time required for a determination by the present method is less than half that required by the method as described by Blasdale.

In conjunction with Dr. H. C. Sherman, at whose suggestion this investigation was undertaken, the modified method has been applied to a number of samples of olive, lard, and other fatty oils, in comparison with the "constants" by means of which such oils are usually judged. The results of this study will be given in a subsequent paper.

QUANTITATIVE LABORATORY,
June, 1903.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 88.]

THE VISCOSITY OF THE SOAP SOLUTION AS A FACTOR IN OIL ANALYSIS.

BY H. C. SHERMAN AND HERBERT ABRAHAM.

Received June 26, 1903.

AS PART of a comparative study, undertaken in this laboratory, of some of the so-called analytical constants, we have determined

the viscosities of solutions of the potassium soaps of several vegetable and a few animal oils. The method of making this viscosity test¹ and the principal conditions which influence the results have been fully described by one of us.¹ In the present paper, we give the figures obtained by the method as finally adopted, and compare them with some of the more commonly determined constants.

The specific gravities and iodine absorption (Hübl) figures were determined as in previous investigations.² The figure here called "Specific Maumené" is the rise of temperature produced on mixing 10 cc. of sulphuric acid with 50 grams of the oil, the result expressed in percentage of the rise shown by 50 grams of water under the same conditions.³ The reaction was carried out in small, jacketed beakers, ordinary "C. P. concentrated" acid being used, except in cases where the reaction became too violent, when acid of about 89 per cent. was substituted, as noted below.

All of the olive oils tested were purchased from presumably reliable dealers in New York City and are believed to be pure, though some are cheap oils of rather poor quality. With the exception of No. 18, all of the samples of lard oil, cottonseed and maize, and the first sample of linseed were sent to us by the makers as pure typical specimens. The remaining samples were purchased from responsible dealers and are believed to be pure. The dates given in the table indicate the years in which the samples were obtained by us.

The results obtained are shown in the following table:

VISCOSITY FIGURES AND OTHER CONSTANTS OF SOME FATTY OILS.

No.	Description of oil.	Sp. gr. 15.5°.	Hübl figure.	Specific Maumené.	Viscosity figure.
1	Olive, "Lucca," 1903	0.9144	79.7	88	168.4
2	Olive, "Marseille," 1903	0.9152	82.3	91	168.0
3	Olive, "Niece," 1903	0.9156	81.5	88	174.6
4	Olive, "Bordeaux," 1903	0.9158	81.0	88	135.5
5	Olive, "Bordeaux," 1903	0.9160	81.6	88	185.7
6	Olive, "California," 1903	0.9160	86.0	93	180.0
7	Olive, "Bordeaux," 1903	0.9162	80.6	87	174.4
8	Olive, "Marseille," 1903	0.9162	83.9	97	145.8
9	Olive, "Lucca," 1901	0.9165	80.5	..	165.8
10	Olive, "Bordeaux," 1903	0.9165	84.5	100	151.9
11	Olive, unknown origin, 1899 ..	0.9170	84.5	100	153.7
12	Olive, unknown origin, 1903 ..	0.9171	81.5	89	168.0

¹ See the preceding paper.

² This Journal, 23, 168.

³ This Journal, 24, 266-273.

VISCOSITY FIGURES AND OTHER CONSTANTS OF SOME FATTY OILS.—

(Continued).

No.	Description of oil.	Sp. gr. 15.5°.	Hübl figure.	Specific Maumené.	Viscosity figure.
13	Olive, unknown origin, 1901 ..	0.9177	86.1	106	157.9
14	Lard oil, first quality, 1903	0.9165	72.1	92	135.0
15	Lard oil, second quality, 1903..	0.9181	74.2	99	133.1
16	Lard oil, third quality, 1903 ...	0.9187	63.9	79	126.9
17	Lard oil, best commercial, 1900	0.917	73.3	106	122.9
18	Lard oil, for lubricating, 1899 .	0.919	72.5	88	128.1
19	Almond, commercial, 1899	0.919	98.1	114	167.8
20	Arachia, commercial peanut, 1899	0.917	105.9	176	126.6
21	Castor, crystal, 1899	0.964	86.9	94	126.6
22	Cotton, prime summer yellow, 1900	0.920	102.8	161	127.9
23	Cotton, choice summer white, 1900	0.923	105.2	171	126.6
24	Cotton, old sample	0.926	103.3	197 ¹	126.6
25	Rape, commercial, 1901	0.920	107.4	144 ¹	125.6
26	Rape, unknown origin.....	0.920	108.6	...	125.7
27	Rape, unknown origin, old....	0.926	99.3	...	124.7
28	Blown rape, commercial, 1901 .	0.974	56.6	...	123.2
29	Sesame, commercial, 1899	0.924	105.3	158	139.2
30	Maize, from glucose works, 1900	0.924	117.2	174	126.6
31	Poppy, unknown origin	0.925	125.3	212 ¹	123.9
32	Linseed, from Dakota seed, 1900	0.934	180.1	300 ¹	126.6
33	Linseed, commercial, 1898.....	0.938	177.1	298 ¹	126.6

COMPARISON OF VISCOSITY FIGURE WITH OTHER CONSTANTS.

The olive oils in the table are arranged in the order of their specific gravities and it will be seen that, with few exceptions, the increasing specific gravity is accompanied by increasing iodine absorption of Maumené figures, while the viscosity figure, as a rule, decreases. This may be shown by averaging separately the samples falling in the first and second halves as given in the table. The results are:

	Specific gravity.	Hübl figure.	Specific Maumené.	Viscosity.
Average, Nos. 1-7..	0.9156	81.8	89	176.7
Average, Nos. 8-13.	0.9168	83.5	98	157.2

The first group gives average figures which would indicate purity and high quality, and here the viscosity figures are high. The second group gives results which would be taken as indicating a lower quality of oil, and here the viscosity figures average much lower. It is interesting to note in this connection that five of the

¹ Determined by the use of acid of about 89 per cent.

seven samples in the first group were commercially rated as extra high grade, and that four of the six samples in the second group were cheap oils.

Comparing samples Nos. 14, 15 and 16, lard oils of first, second and third quality from the same maker, it appears that here also the viscosity figure decreases with the quality of the oil, though the differences are too small to be of much significance.

Comparing olive oils with other oils, the only one of the latter examined by us which equals olive in its viscosity figure, is almond oil with a figure of 167.8. Next below comes sesame with a figure of 139.2. Blasdale¹ has already stated that almond equals, and sesame approaches, olive oil in this respect. We have, however, been unable to confirm his statement that rape oil gives a soap solution of as high viscosity as that of olive oil. The high result obtained by Blasdale may be due to the fact that he used a fixed amount, instead of a fixed excess, of alkali for saponification. This procedure would, of course, leave a larger amount of uncombined alkali in the case of rape than with the other oils, and this larger excess of alkali would increase the viscosity of the soap solution. We have not examined mustard-seed oil, which according to Blasdale yields a soap solution of very high viscosity.

All of the samples examined by us, other than olive, almond and sesame oil, showed viscosity figures between 122 and 135. It seems remarkable that this figure should show such slight variations between oils differing so markedly in other properties as, for example, lard, linseed and castor oils.

From the results obtained with castor and with blown rape-seed oils, it is evident that the viscosity of the soap solution is independent of the viscosity of the oil itself.

Our results fully confirm the conclusion reached by Blasdale that the adulteration of olive oil with any other oil likely to be used for the purpose would result in a lowering of the viscosity figure. The following experiments were designed to determine whether the viscosity figure actually found in such a mixture would agree with that calculated from the constituents. Soap solutions of lard, cottonseed, and peanut oils were mixed in different proportions with those of olive oil and the viscosities determined with the following results:

¹ This Journal, 17, 940.

MIXTURES OF SOAP SOLUTIONS OF OLIVE AND OTHER OILS.

Nature of soap solution.	Viscosity figure.	
	Found.	Calculated.
Olive oil	168.4
Lard oil.....	128.1
$\frac{3}{4}$ olive, $\frac{1}{4}$ lard oil.....	158.6	158.4
$\frac{1}{2}$ olive, $\frac{1}{2}$ lard oil	147.6	148.2
$\frac{1}{4}$ olive, $\frac{3}{4}$ lard oil.....	137.8	138.2
Peanut (arachis) oil	126.6
$\frac{3}{4}$ olive, $\frac{1}{4}$ peanut oil	143.6	158.0
$\frac{1}{2}$ olive, $\frac{1}{2}$ peanut oil	134.2	147.5
$\frac{1}{4}$ olive, $\frac{3}{4}$ peanut oil	129.0	137.1
Cottonseed oil.....	127.9
$\frac{9}{10}$ olive, $\frac{1}{10}$ cottonseed oil	152.0	164.4
$\frac{3}{4}$ olive, $\frac{1}{4}$ cottonseed oil	142.6	158.3
$\frac{1}{2}$ olive, $\frac{1}{2}$ cottonseed oil	132.1	148.2

From this table it appears that mixtures of olive and lard oils give practically the calculated results, while the viscosities of mixtures of olive with cottonseed or peanut oils are lower than would be calculated from the viscosities and proportions of the oils in the mixture. Hence the adulteration of olive with cottonseed or peanut oil produces a greater change in the viscosity figure than that which would have been predicted.

A somewhat similar, but more striking result was obtained from the examination of mixtures of soap solutions of pure fatty acids. Such mixtures also give viscosities lower than would be calculated. Three grams of lauric acid, treated in the same manner as described for fatty oils, gave a viscosity figure of 126.6, oleic acid gave a figure of 239.7, while stearic acid yielded a soap solution too viscous to be tested at ordinary temperatures. Yet large proportions of the oleate or stearate solution could be added to the laurate solution without appreciably increasing its viscosity.

INFLUENCE OF ATMOSPHERIC OXIDATION.

In view of the fact that even the so-called non-drying oils may undergo sufficient oxidation from simple exposure to air to affect seriously the "constants" usually determined in oil analysis,¹ it is of some importance to determine the effect of such oxidation upon the viscosity figure. Speaking generally, it appears that the effect of sufficiently prolonged exposure is to cause olive and almond oils to lose their characteristic high viscosity figures while those oils whose figures are lower are but little affected. A sample of olive oil exposed in an uncorked bottle for several months

¹ This Journal, 2, 711.

showed a loss of 7 units in the Hübl figure and of 25 units in the viscosity figure. An almond oil, similarly exposed for a longer time, decreased from 98.1 to 84.6 in the Hübl figure and from 167.8 to 123.8 in the viscosity figure. On the other hand, a sample of lard oil exposed until the Hübl figure fell from 73.3 to 66.7 showed no appreciable change in the viscosity figure; and in several samples of cottonseed, maize and linseed oils, in which atmospheric oxidation had caused losses of 10 to 40 units in the Hübl figures, the decrease in the viscosity figure was in no case greater than 4 units.

SUMMARY.

Olive and almond oils yield soap solutions of considerably greater viscosity than those obtained from the other more common fatty oils.

This "viscosity figure" is apparently higher in the better than in the poorer grades of olive oil.

The lowering of the viscosity figure by admixture of other oils furnishes an additional method for the detection of adulteration in olive and almond oils. As suggested by Blasdale, it will be especially useful for the detection of lard oil for which we have no specific test. The characteristic high viscosity figure of olive or of almond oil may be largely lost on sufficiently long exposure of the oil to air at ordinary temperature.

While the reason for the high figures shown by olive and almond oils cannot be stated, it appears probable that the explanation is to be found in the quantitative relations of the fatty acids present, rather than in the presence of any peculiar constituent, and that interesting results might be obtained from a study of the viscosities of the soap solutions of pure fatty acids and their mixtures.

QUANTITATIVE LABORATORY,
June, 1903.

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION
OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

THE DETERMINATION OF COMMERCIAL GLUCOSE IN MOLASSES, SYRUPS, AND HONEY.

BY ALBERT E. LEACH.
Received May 26, 1903.

THE importance of a ready method for the determination of so common an adulterant as commercial glucose is obvious. Several

of the states have in their food laws a provision requiring that so called "compound" foods (such as molasses containing commercial glucose), to be legally sold, must have formulas setting forth the names and percentages of their ingredients. In such cases it becomes virtually a necessity for the analyst to be able to verify, within certain limits, such formulas and thus guard against fraudulent and misleading statements thereon.

Unfortunately, from the variability in composition of commercial glucose, there can obviously be no accurate method for its determination, especially in complex, saccharine products in which one is likely to find it, and which themselves contain components common to glucose.

In enforcing the food laws conservatively, a formula on a package expressing the name and percentage of ingredients in the food contained therein is not condemned, because it differs by a few per cent. only from the analyst's findings, nor should the presence of a mere trace of an adulterant, which may be accidental, serve as a basis for a complaint in court. It is only when substantial deviations from a manufacturer's formula are found, or the presence of enough of the adulterant is evident to make it an object for fraudulent use, that the analyst should condemn it. In cases like these, an approximate method must be used, but preferably one, the adaptability of which to the purpose in hand has been well tested by long trial.

In molasses, syrups, honey, and similar preparation wherein commercial glucose is present as an adulterant, it has been the practice of the writer for upwards of ten years in the prosecution of such cases under the food laws of Massachusetts to calculate the approximate amount of commercial glucose present by assuming 175 as the direct polarization of a normal weight of the glucose, 26.048 grams, made up to 100 cc. and polarized in a 200 mm. tube. From this was naturally developed the formula which was long afterwards included by the writer in the methods outlined by him as an associate referee for the analysis of saccharine products, and later incorporated in the provisional food methods of the Association of Official Agricultural Chemists,¹ as follows:

$$G = \frac{(a-S) 100}{175},$$

where G = per cent. of commercial glucose in the sample,

¹ Bureau of Chemistry, Bulletin 65, p. 48.

a = direct polarization of sample, and S = per cent. of cane-sugar as calculated from direct and invert polarization according to Clerget. This method and formula have been severely criticised by Mr. Edward Gudeman,¹ who regards the use of a single assumed factor as unwarranted, and one object of the present paper is to reply to his criticism and to show how satisfactorily the method has proved in practice. The formula applies more particularly to molasses and maple-syrup, as stated in the provisional methods. For honey, the same factor, 175, is used, but more accurate results are obtainable by dividing the polarization of the sample at 87° by this factor.

When asked in court, as one is sure to be in a contested case, the amount of commercial glucose in the sample, it is convenient to reply that *at least* such and such an amount must necessarily be present. By assuming in the above formula the highest figure that is apt to be found as the direct polarization of commercial glucose (175), it is obvious that the resulting value for S is the lowest or minimum one, thus giving the benefit of any doubt to the defendant. In other words, it is perfectly safe to allege that amount of glucose.

Realizing the uncertain composition of commercial glucose due to variations in amount of dextrose, maltose, dextrine and water present therein, the above method of calculation was long regarded by the writer as of doubtful value on theoretical grounds, and was not published for several years after being used. Continued opportunities were furnished, however, for comparison of the results thus calculated with actual conditions prevailing, such for example as occasional recipes furnished by defendants in court showing how the products were mixed, and one could hardly fail to be impressed by the striking and almost invariable similarity in results. Longer experience produced greater confidence, and it was thought best to examine a number of samples of commercial glucose obtained in a variety of ways from confectioners, mixers of compound honey and molasses, and jelly and jam manufacturers, with a view to ascertain the grades actually used by them and hence best suited for their purpose. It was found that considerable uniformity prevailed in the character of the glucose employed for different uses, especially as regards polarization. Thus seven

¹ Proceedings of 19th Annual Convention of the Association of Official Agricultural Chemists, Bur. of Chem., Bull. 73, p. 65.

samples, obtained in 1893, 1898 and 1901 from as many different manufacturers of compound molasses and honey or from dealers supplying them, polarized as follows:¹ 173°, 171°, 176°, 175°, 178°, 168° and 177°, the average being 174°. The writer's experience is not in accord with Mr. Gudeman's, who states that he has never known the manufacturer of glucose to furnish special or uniform grades for special purposes. In this connection the following is in point from the letter of a kind friend who obtained, through a broker, samples of glucose for analysis and who quotes from the broker's letter: "I am sending you two samples of glucose from the factory with the following advice: 42° Bé. is the grade used for syrup and honey, the XXXXX is the grade used for chewing-gum." The latter grade was found to polarize at 184.6°.

Another letter from a molasses mixer, who labels his product correctly under the law, runs as follows: "Only one kind of glucose is used in this kind of mixture, a sample of which we send you, called in the trade mixing or "M" glucose; the gravity we believe is somewhere about 42° Bé."

The molasses mixer naturally prefers the grade of glucose which, by its consistency, is best adapted without further treatment for mixture with his product. If it is too heavy in body, it must first be watered, and again if too thin it is equally unfit for direct use. Commercial glucose of 42° Bé. in density is admirably suited to his purpose, and this is the grade that more often polarizes from 170° to 175°. A number of samples obtained from confectioners and makers of compound jellies and jams were found to polarize from 150° to 157°.

Out of eleven samples of commercial glucose used for a variety of purposes in food and obtained from manufacturers of these foods, but one sample was found to polarize above 178° (the "XXXXX" brand above referred to), and none below 150°. Doubtless wider variations may possibly occur in commercial glucose of different densities as found on the market, but the point made here is that only such grades as are adapted for the particu-

¹ Figures being expressed in terms of 26.048 grams glucose made up to 100 cc. with water and polarized in a 200 mm. tube on the cane-sugar scale of the S. & H. instrument. It should be noted that in polarizing glucose, or molasses and syrups adulterated therewith, a 100 mm. tube should be used and the necessary correction applied, in order to bring the high reading within the limits of the scale. For exact data as to clarification of sample and other precautions, the reader is referred to Bull. 65. Bureau of Chemistry, p. 47.

lar purpose in hand are used by the food manufacturer, and these come within certain particular limits.

Mr. Gudeman's deductions regarding the composition and variations of glucose show his familiarity with its manufacture, but he makes no mention of the effect of maltose as one of the important reducing sugars present, though he apparently makes allowance for it in a process which he suggests as an alternative to the provisional method. In this process he estimates the reducing sugars before and after inversion, and again after hydrolyzing with malt extract, calculating by difference the dextrose resulting from the hydrolysis of the non-reducing substances. In making the latter calculation, he assumes a factor which can be true only of a fixed proportion of maltose to dextrine, a condition which cannot, of course, be depended on. Another source of error in Gudeman's method lies in the fact that his results are expressed in percentage of dry substance, leaving one in the dark as to the actual amount of glucose present as an adulterant, unless one assumes also a definite percentage of water in the glucose. A determination of dry grape-sugar or dextrose in molasses or honey is of no importance whatever to the enforcer of the food law.

Mr. Gudeman seeks to prove the unreliability of the provisional method by applying it to various hypothetical mixtures of grape-, cane- and invert-sugar, for which the method never was intended and could not, under any possible conditions, be used. The provisional method applies solely to molasses and syrups as found on the market, and to the commercial glucose used as an adulterant. No ambiguity need attend the use of the term commercial glucose in this country. The product has too important a place in trade not to be a pretty well understood article. By it is not meant a mere haphazard mixture of dextrose, maltose and dextrine, but a well-defined series of graded products of varying density, depending on the degree of conversion, but which, as the result of long experience in manufacture, are fairly uniform, so that the product of a given grade or density has a polarization varying between narrow limits. While the confectioner from his multiplicity of products can use various grades, the honey and molasses mixer is limited to the use of a special grade best suited to his use.

In carrying out the provisional method, commercial glucose is considered as just as much of an entity as milk, for example. To cite a parallel case, it has long been a successful practice for the

food analyst to approximately calculate the amount of added water in milk by using an assumed constant for a factor, as for instance, the per cent. of solids not fat or total solids, in spite of the well-known wide variation in the normal constituents in milk. It is equally legitimate to adopt a constant for calculation of commercial glucose, based on such a uniform factor as the polarization seems to be in such cases.

Not the least of the advantages of the method is its simplicity, requiring only a direct and invert reading of the sample, which must be done in any event before deciding on the presence of commercial glucose. The method has never been claimed to be exact, but continued experience shows it to yield results much nearer the truth than was at first supposed possible.

Molasses, table syrup, and honey, put up in packages having incorrect formulas thereon, are included in the lists of adulterated brands, which, under the law, the Massachusetts Board of Health is obliged to publish monthly. The calculation of glucose in these cases is always based on the use of 175 as a factor, and experience has shown that manufacturers who doubt the findings of the Board are not slow to challenge its results.

Finally, the method has never been discredited, after long usage in the Massachusetts courts, where, of all places, in closely contested cases it is naturally subject to any criticism that may reasonably be brought against it.

PURIFICATION AND ESTIMATION OF IODINE.¹

BY ABRAHAM GROSS.

Received July 7, 1903.

IN VIEW of the importance of iodine in the arts and of the apparent difficulty in obtaining it absolutely pure, a discussion of this subject does not appear untimely and may prove of some value. Very few methods have been published in the direction of iodine purification and but one finds favorable mention. This is the method used by Stas in his researches on the atomic weight of iodine, and consists in dissolving iodine in a solution of potassium iodide, precipitating the iodine with water, drying over calcium nitrate, and subliming the dried mass. This method is criticized

¹ Read before the Pittsburg Section, June 18, 1903.

by Lean and Whatmough,¹ who state that pure iodine can be obtained by heating cuprous iodide in dried air at 240° C. when the iodine is liberated.

Other investigations on this subject have been made by C. Meineke² and Z. Musset.³ With a desire to obtain a reliable method for purifying iodine it was considered advisable to test the efficacy of the Stas method, and to compare the purity of the iodine thus produced with that obtained by other methods which suggested themselves at the time.

Accordingly, the following methods were tried: (1) The Stas method; (2) washing iodine with water, drying a portion over sulphuric acid, another portion over calcium nitrate and a third portion over calcium chloride; (3) mixing iodine with potassium iodide and drying over sulphuric acid.

Each of the above was then sublimed three times after drying.

The first method was carried out according to the directions of Stas, who states that to dissolve four kilos of iodine a solution of 1 kilogram of potassium iodide in 1 kilogram of water was required. These proportions were found inadequate, for, after standing some time with frequent shaking, a considerable portion of the iodine remained undissolved.

Several additions of potassium iodide and water were made, until complete solution was effected. This was accomplished when the proportions were 4 of iodine to 2 of potassium iodide and 2 of water.

The solution of iodine was then poured into water and allowed to stand until all of the iodine was precipitated. The supernatant fluid was poured off and the iodine washed with water until free from potassium iodide. It was then brought upon a filter, with sand as a filtering medium, and the water withdrawn by suction. The iodine was then transferred to a shallow dish and dried over calcium nitrate, which was replaced as soon as affected by the moisture. The drying continued twelve days. The dried sample was then sublimed three times by a process which will be described later.

In the next three methods, the iodine was washed with water fifteen times, and, after as much water as possible had been withdrawn by suction, was divided into three portions and dried, as

¹ *J. Chem. Soc. (London)*, 1899.

² *Chem. Ztg.*, 16, 1219.

³ *Ztschr. anal. Chem.*, 1891, p. 45.

previously mentioned, over sulphuric acid, calcium nitrate and calcium chloride respectively.

In conducting this experiment, two other points were in view: (1) To determine the best drying agent; (2) to ascertain whether any chlorine would be set free and absorbed by the iodine when the sample was dried over calcium chloride.

It may be mentioned here that the calcium nitrate and sulphuric acid were equally efficient as drying agents, but the inconvenience of constantly changing the calcium nitrate rendered it less desirable. Each of these samples was then sublimed three times.

The fifth sample was prepared by mixing iodine with pure potassium iodide, drying over sulphuric acid and subliming three times. The iodine obtained by this method was discarded, as a white residue remained after each sublimation. Apparently the potassium iodide was carried over with the iodine vapor.

PROCESS OF SUBLIMATION.

The iodine prepared by the methods previously described was placed in a piece of combustion tubing slightly inclined and resting on a support. Following the iodine was a plug of ignited asbestos to prevent the heated iodine from running down the tube. The lower end of the tube was connected to two tubes containing phosphoric anhydride and one containing calcium chloride. In this manner the air drawn through was perfectly dry. The upper end was covered by a bottle fitted to a rubber stopper to catch any vapor not previously condensed.

Through the stopper passed a glass tube which connected with an empty jar as a precautionary measure and in turn with a cylinder containing water and with the suction-pump. The suction was regulated by the bubbles produced in the cylinder. To prevent any accident from too sudden heating, a piece of iron pipe was placed over that part of the tube containing the asbestos and iodine and extending beyond for about 4 inches. This was protected from the glass by asbestos. A gentle heat was used and enough suction applied to condense the vapor sufficiently far away from the pipe to prevent any liquefaction of the sublimed crystals.

The succeeding two sublimations were conducted in precisely the same manner.

The following method proved itself highly satisfactory in the

determination of the purity of iodine. About 2 grams of the iodine were placed in a flask, 40 cc. of water, and about 4 grams of shot-zinc added. The flask was then shaken and allowed to stand with stopper inserted until the fluid was colorless. When all the iodine was taken up by the zinc, the solution was filtered into a half-liter flask, the residue and zinc hydroxide washed with hot water until free from iodine and the fluid made up to 500 cc. Fifty cc. of the solution were placed in a porcelain dish and titrated with silver nitrate, with potassium chromate as an indicator, until the end point, a slight brownish color, was reached.

The following results were obtained: Stas method—mean of five determinations gave 100.02 per cent.; second method—mean of five determinations gave 99.65 per cent. A sample of unpurified iodine gave, by this method, 98.83 per cent.

The iodine dried over the calcium chloride was tested for chlorine according to Fresenius,¹ but none was found.

For comparison, a sample of unpurified iodine was tested by the same method and the presence of the chlorine was indicated.

The following summary may be deduced from the foregoing research: (1) The Stas method gave the purest iodine; (2) sulphuric acid was the best drying agent; (3) the iodine was not contaminated when dried over calcium chloride; (4) the iodine, when pure, was satisfactorily determined when converted into zinc iodide and titrated with silver nitrate, with potassium chromate as an indicator.

A COLORIMETRIC METHOD FOR THE DETERMINATION OF SMALL QUANTITIES OF POTASSIUM.

BY LUCIAN A. HILL.

Received July 11, 1903.

THIS method is primarily intended for use in the analysis of soil extracts and drainage waters where the potassium is in such small quantities that it is impracticable to use a gravimetric method. It has been used in this laboratory on a number of soil extracts, and has given very satisfactory results.

¹ "Qualitative Analysis."

The method depends upon the precipitation of the potassium in the usual way with chlorplatonic acid, and the subsequent reduction of the potassium chlorplatinate with stannous chloride in the presence of free hydrochloric acid. The precipitate of potassium chlorplatinate in very dilute solution is, of course, very small, consisting of a few minute crystals. A distinct color is imparted to the solution on adding the stannous chloride solution, however, even though the original solution contained not more than one part of potassium oxide per million.

SOLUTIONS REQUIRED.

Standard Potassium Chlorplatinate.—0.518 gram of potassium chlorplatinate is dissolved in water and the solution made up to 100 cc. For use, 1 cc. of this solution is diluted to 100 cc. One cc. of the diluted solution is equivalent to 0.00001 gram potassium oxide.

Stannous Chloride.—Boil 75 grams of powdered or granulated tin with 400 cc. of concentrated hydrochloric acid in an Erlenmeyer flask until nearly all of the tin is dissolved. Keep in a tightly stoppered bottle over a small piece of tin.

Analytical Process.—The analytical process, up to the point of adding the stannous chloride, is essentially the same as that used in ordinary analysis.

To 50 cc. of the solution to be tested add 1 cc. of dilute sulphuric acid, evaporate to dryness, and ignite to whiteness. Dissolve the residue in hot water, acidified with a few drops of hydrochloric acid, and add an excess of chlorplatonic acid. The solution is then evaporated to a thick paste in a small dish and 80 per cent. alcohol added. Wash the precipitate thoroughly with 80 per cent. alcohol, then dissolve in boiling water, cool, and make up to a definite volume (100 or 200 cc.).

Transfer 50 cc. of this solution to a color-comparison cylinder and add 3 cc. of the stannous chloride solution. A yellow color is produced, the intensity of which is proportional to the amount of potassium chlorplatinate present. This color is exactly matched by introducing into other cylinders quantities of the standard potassium chlorplatinate solution and 3 cc. of the stannous chloride solution, as before. Below are given results obtained by this method:

Amount K_2O added. Parts per million.	Amount K_2O recovered. Parts per million.
1..... 1.0	0.92
2..... 1.0	0.8
3..... 1.0	1.0
4..... 1.0	1.2
5..... 2.0	1.9
6..... 2.0	2.1
7..... 2.0	2.0
8..... 2.0	2.0
9..... 3.0	3.2
10..... 3.0	3.2
11..... 3.0	2.8
12..... 3.0	2.8
13..... 4.0	4.4
14..... 4.0	4.0
15..... 4.0	4.0
16..... 4.0	4.4
17..... 5.0	5.0
18..... 5.0	5.0
19..... 5.0	4.9
20..... 10.0	11.6
21..... 10.0	11.2

NEW HAMPSHIRE COLLEGE,
AGRICULTURAL EXPERIMENT STATION.

THE DELICACY OF TESTS EMPLOYED FOR THE DETECTION OF METALS.

BY FLORENCE JACKSON.

Received June 24, 1903.

THE work in the following paper was undertaken for the purpose of determining the comparative delicacy of the tests employed in the ordinary methods used in qualitative analysis in detecting metals. To this end, solutions of salts were made of such strength that 1 cc. of the solution contained 5 mg. of the element under consideration or 1 part in 200. The weaker solutions were made from the standard by diluting with distilled water. When (as in the case of silver chloride) ammonia present in the water might exert a solvent influence, water free from ammonia was used. The reagents used were of the strength employed in the Wellesley College Chemical Laboratory (see table at the end), and were added drop by drop to 1 cc. of the solution under consideration.

The experiments were carried through twice, new standard solu-

tions being used the second time and, in cases of discrepancy, further tests were made.

The figures under the "final tests" were chosen as the probable limit of detection, if the element was not known to be present. They do not, therefore, usually represent the extreme limit indicated under the experimental conditions of this paper. This may account for the discrepancy between my figures and those given by other authorities.

FINAL TESTS. SUMMARY BY REAGENTS.

(A) HCl.

(a) Sp. gr. 1.035

		1 : 1,000,000.	Comey. Mulder.
Ag	1 : 64,000	1 : 378,000.	Harting.
		1 : 200,000.	Lassaigue.
		1 : 189,000.	Pfaff.
Hg ^I	1 : 16,000	1 : 327,000.	Fresenius.
Pb	1 : 500	1 : 1,077.	Wormley.

(b) Sp. gr. 1.1 As above except

Hg^I 1 : 8,000

(B) NaCl.

Ag	1 : 32,000
Hg ^I	1 : 15,000
Pb	1 : 1,000

(C) H₂S.

As ^{II}	1 : 1,024,000	1 : 13,200.	Wormley.
Sb	1 : 512,000	1 : 24,000.	Wormley.
Bi.Ag.Sn ^{II}	1 : 64,000		
As. ^V Hg. ^I Sn ^{IV}	1 : 32,000	As 1 : 1530.	Wormley.
		{ Pb 1 : 1,000,000.	Prescott and Sullivan.
		1 : 26,900.	Wormley.
		{ Hg ^{II} 1 : 46,000.	Green coloration { Las-
		1 : 23,000.	Brown " saigne.
		1 : 6,770.	Wormley.
		{ Cu 1 : 100,000.	Prescott and Sullivan.
		1 : 12,500.	Wormley.

(D) NH₄OH.

	Mn	1 : 64,000	
	Mg	1 : 32,000	
	Co.Fe. ^{III} Pb	1 : 16,000	
Al.Bi.Cu.Fe. ^{II} Hg. ^{I-II} Sn. ^{II} Zn	1 : 8,000	Hg ^{II} 1 : 13,500.	Wormley.
	Cu	{ 1 : 20,000.	Prescott and Sullivan.
		1 : 12,500.	Wormley.
	Zn	1 : 12,500.	Wormley.
	Cd.Cr.Ni.Sn ^{IV}	1 : 4,000	
	Sb	1 : 1,000	1 : 1,200. Wormley.
Ag.(NH ₄ OH 1 : 10)		1 : 500	

(E) NaOH.

Mn	1 : 128,000		
Fe ^{III}	1 : 32,000		
Al.Cu.Co.Hg. ^I Ni	1 : 16,000	Cu	1 : 125,000. Wormley.
NH ₃ .Bi.Cr.Fe. ^{II} Ag	1 : 8,000		
Cd.Zn	1 : 4,000		
Sn ^{II-IV}	1 : 2,000		
Sb	1 : 1,000	1 : 1,200.	Wormley.
Pb.Hg ^{II}	1 : 500	Hg ^{II}	1 : 677. Wormley.

(F) K₂CrO₄.

Ba	1 : 256,000		
Pb	1 : 32,000	{ 1 : 111,982. Harting.	
		{ 1 : 107,700. Wormley.	
Cu	1 : 16,000	1 : 50,000.	Wormley.
Ag	1 : 8,000		
Bi.Hg ^I	1 : 4,000		
Cd	1 : 1,000		
Hg ^{II}	1 : 333		
Sr	1 : 200		

(G) KI.

Ag.Cu.Pb.Hg ^I	1 : 8,000	{ Ag 1 : 47,250. Harting.	
		{ Pb 1 : 21,540. Wormley.	
		{ Cu 1 : 12,500. Wormley.	
Hg ^{II}	1 : 2,000	1 : 3,380.	Wormley.

(H) Na₂HPO₄.

Mg	1 : 128,000	(Addition of NH ₄ Cl and NH ₄ OH.)
Ca	1 : 16,000	
Ag.Sr	1 : 8,000	
Ba	1 : 4,000	

(I) (NH₄)₂S.

Co	1 : 512,000	1 : 309,000. Pfaff.
Fe ^{II-III}	1 : 128,000	
Ni	1 : 64,000	
Al.Cr.Mn.Zn	1 : 8,000	

(J) H₂O.

Sb	1 : 2,000
Bi	1 : 4,000

(K) Na₂CO₃.

Sr	1 : 64,000		
Bi.Mn.Ag	1 : 32,000		
Cu.Fe. ^{III} Hg. ^I Ni	1 : 16,000	Cu	1 : 12,500. Wormley.
Al.Ba.Co.Fe. ^{II} Zn	1 : 8,000	Zn	1 : 12,500. Wormley.
Cd.Ca.Cr.Pb.Mg	1 : 4,000	Pb	1 : 53,850. Wormley.
Hg ^{II}	1 : 250		

(L) H₂SO₄.

Ba	1 : 256,000	1 : 79,300. Harting.
Pb	1 : 16,000	1 : 21,540. Wormley.
Sr	1 : 8,000	1 : 23,100-25,200. Fresenius.
Ca	1 : 2,000	
Hg ^I	1 : 1,000	

(M) SnCl_2 .			
	Hg^{I}	1 : 32,000	
	Hg^{II}	1 : 16,000	1 : 13,500. Wormley.
(N) KCN.			
	Co	1 : 16,000	
	Cu.Ni	1 : 2,000	
	Cd	1 : 1,000	
(O) $\text{K}_4\text{Fe}(\text{CN})_6$.			
	Fe^{III}	1 : 64,000	
	Fe^{II} Pb	1 : 32,000	Pb 1 : 10,770. Wormley.
	Cu	1 : 16,000	{ 1 : 100,000. Prescott and Sullivan. 1 : 31,250. Wormley.
(P) $(\text{NH}_4)_2\text{CO}_3$.			
	Sr	1 : 16,000	1 : 95,200. Comey.
	Ca.Co. Fe^{III}	1 : 8,000	Ca 1 : 163,000. Fresenius.
	Ba. Fe^{II}	1 : 4,000	Ba 1 : 201,000. Fresenius.
	Mg	1 : 200	
(Q) $(\text{NH}_4)_2\text{C}_2\text{O}_4$.			
	Ca	1 : 64,000	
	Sr	1 : 32,000	
	Ba	1 : 2,000	
(R) CaSO_4 .			
	Ba	1 : 64,000	
	Sr	1 : 1,000	
(S) H_2SiF_6 .			
	Ba	1 : 2,000	
	K	1 : 200	
	Na	1 : 143	
(T) H_2PtCl_6 .			
	NH_3	1 : 2,000	
	K	1 : 200	

STRENGTH OF REAGENTS EMPLOYED.

$(\text{NH}_4)_2\text{CO}_3$	175 grams to a liter + 100 cc. concentrated NH_4OH .
NH_4OH	Diluted 1 : 3 and 1 : 10.
$(\text{NH}_4)_2\text{C}_2\text{O}_4$	40 grams to a liter.
$(\text{NH}_4)_2\text{S}$	Saturate NH_4OH (0.96) with H_2S .
HCl.....	Sp. gr. 1.12 and 1.035.
HNO_3	Sp. gr. 1.2.
H_2SO_4	Diluted 1 : 5.
H_2S	From Kipp generator. Washed in H_2O .
HgCl_2	25 grams to a liter.
MgSO_4	50 " " " "
K_2CrO_4	50 " " " "
KCN.....	50 " " " "
KCNS.....	5 " " " "
$\text{K}_4\text{Fe}(\text{Cn})_6$	75 " " " "
KI.....	25 " " " "
Na_2CO_3	250 " " " " Crystallized salt.
NaCl	50 " " " "
NaOH	150 " " " "
Na_2HPO_4	50 " " " "
SnCl_2	Sn dissolved in HCl + 4 parts of H_2O .

The results obtained from these experiments agree, in general, with facts already known. The work has value chiefly, as it seems to me, in the collection of definite data for future investigation rather than in any new facts brought to light by the figures given.

WELLESLEY COLLEGE,
June, 1903.

A LECTURE EXPERIMENT WITH AN UNDISSOCIATED SALT.

By D. MCINTOSH.

Received June 18, 1903.

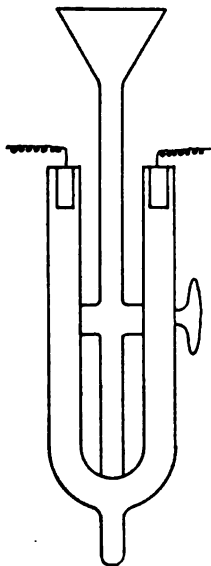
WHEN a sulphocyanate is added to a ferric salt, the deep red color produced is thought, for a number of reasons, to be due to the undissociated ferric sulphocyanate. These may be briefly stated: First, neither the ferric nor the sulphocyanate ion is colored; second, the crystals of ferric sulphocyanate, which can contain no ions, are similarly colored; third, in ether, in which salts are but slightly dissociated, the color is unchanged; fourth, an excess of a sulphocyanate increases the color, while the addition of sulphate ions weakens it.

If, then, ferric sulphocyanate were placed in a tube between two layers of a colorless liquid, the passage of a current should not increase the rate of diffusion; if, on the other hand, the color were due to a complex cation or anion, the color should move either to the cathode or anode.

If a solution of ferric sulphocyanate be placed in a U-tube, and carefully covered over with a less dense electrolyte (dilute hydrochloric acid), a current of $\frac{1}{100}$ ampere may be passed through it for several hours without the relative positions of the color-boundaries changing. The experiment can be made quite striking, by arranging in series two other tubes containing¹ potassium copper tartrate covered with dilute potassium hydroxide, and copper sulphate with ammonium hydroxide covered with ammonium hydroxide. In the first case, the color-boundaries remain stationary, while in the second and third they move towards the anode and cathode respectively.

¹ Mamoni; *Ztschr. phys. Chem.*, 29, 301 (1899).

In the figure is shown a U-tube of a convenient pattern, after Nernst. The lighter liquid is introduced first through the side tube. That the color is due to the undissociated salt is confirmed by conductivity and molecular-weight determinations. The conductivities of mixtures of ferric chloride and ammonium sulphocyanate were 20 to 30 per cent. less than their mean conductivities,



while the rise in boiling-point of a mixture of the two salts is always much less than the sum of the rise in boiling-points due to the two substances taken separately.

McGILL UNIVERSITY,
MONTREAL, April 25, 1903.

NOTES.

Note on Carbon Combustion in a Platinum Crucible.—In a recent paper¹ John V. R. Stehman, referring to the writer's special crucible² for carbon combustion, makes the statement that "the prevalent idea regarding his form of apparatus seems to be a fear of the rubber gasket causing error by burning directly or by be-

¹ This Journal, 28, 237.

² *Ibid.*, 28, 227, and 21, 557.

coming hard and brittle, allowing small pieces to drop into the crucible when the stopper is pushed into place."

While it may be admitted that, prior to experience with the apparatus, such a fear is quite natural, the fact is that long use by many most careful chemists has proved this fear to be quite groundless. Even when the lower half of the crucible is hot enough to burn graphite in air, those parts of the apparatus which are in contact with the rubber gasket are so well cooled by the circulating water that the rubber is wholly unaffected. That there is no error from this cause is shown by the fact that the blanks are always under 0.0005 gram and that sharp results are easy to get on standard carbon samples.

However, a rubber band should not be used until it becomes hard and brittle, not so much from fear of rubber falling into the crucible as from the difficulty of getting a perfectly tight joint with the rubber in this condition.

While, therefore, there is no reason to fear the use of rubber, an asbestos gasket may be successfully used in place of it, if desired. For this purpose, cut a paper pattern, about one-half inch wide to fit accurately around the lower part of the stopper and overlapping about one-sixteenth of an inch at the ends. Cut asbestos paper, of the thickness of a rubber band, over this pattern. Soak the asbestos gasket at least twenty-four hours in a large beaker of water to extract all soluble carbonaceous matter; it is said dextrine is used as a binding material. Fit it, while wet, around the stopper, scraping it down carefully where the ends overlap. Saturate the gasket with water and press it, with a turning motion, into the crucible; there is no difficulty in getting a tight joint. Now test a succession of blanks, which, if the soluble carbonaceous matter has been well extracted, will not exceed 0.0005 gram. The asbestos must be well wetted before putting in the stopper and, just before beginning a combustion, it is well to place a few drops of water in excess around the upper part of the crucible. This will make any possible leak visible and will ensure a saturated and tight joint during the course of the combustion. The writer has tried an asbestos gasket with his crucible on carbon determination with results equally as satisfactory as with the rubber gasket. When determining combined water, however, rubber must be used, for wet asbestos is inadmissible and dry asbestos does not give a tight joint.

While on the subject of carbon determination, it may be well to call attention to two other matters of detail. The writer has recently seen copper oxide for combustion which, instead of having the usual dead-black color and porous appearance, had a reddish color and semi-fused appearance and was not as effective as an oxidizer.

The copper oxide for the small brass tube should be as fine as possible (free, of course, from powder), consistent with keeping the tube open and free. In filling the tube, unless special care is taken, the copper oxide particles may become wedged in spots, leaving empty spaces in the tube. The filling should be slow, using only a little copper oxide at a time and testing it constantly with a wire to be sure the tube is full in every part where it is to be heated.

Where water-bottles are used for furnishing the air-pressure it is well to use water in which a little cupric sulphate has been dissolved. The solution is filtered and, being an inhospitable field for bacterial activity, remains clear and free from the carbonaceous gases which are given off from stagnant water in sufficient amount to affect carbon determinations.

PORTER W. SHIMER.

LABORATORY OF P. W. SHIMER, EASTON, PA.

The Color Test in High Carbon Steels.—Parker says of it that it is "liable to great variations";¹ Galbraith that it "should be abandoned";² Tucker, that "its inaccuracy is well recognized";³ Hadfield that "it had long been a matter of knowledge in the Sheffield steel trade, that the color test was apt to give misleading results";⁴ Metcalf in his book "Steel" characterizes it as "the wildest guess work in the best hands." Campbell in his book "The Manufacture and Properties of Iron and Steel," and elsewhere, repeatedly and emphatically expresses distrust of the method.

It is the writer's experience also that the color method as usually carried out is unreliable. The same drillings do not always dissolve to the same shade. This difficulty can only be overcome by the use of two precautions not generally known and practiced.

(1) One gram must be taken.⁵ (2) The acid must, before using,

¹ *Chem. News*, 42, 88.

² *Journal Iron and Steel Institute*, 181, 234.

³ *Ibid.*, 96, 1, 137.

⁴ *Ibid.*, 96, 2, 187.

⁵ Weighed out into a 41 cc. test-tube provided with a mark at 25 cc. Twenty cc. acid is used for solution. After cooling, the liquid is diluted to the mark, mixed by placing the thumb over the tube and inverting a number of times, and 5cc. withdrawn for comparison.

be made ice-cold by immersing a beaker of it in a larger beaker of ice and water for some time; it must be added all at once, and, instead of simply having the test-tube stand in cold water, it must be moved rapidly and vigorously around in a large beaker of ice-water for a minute after the addition of the acid, and before standing in the water-bath filled with cold (not necessarily ice-cold) water.¹ Dissolving in this way, no violent action takes place; loss of hydrocarbon gas is avoided—or if there is loss, it is a uniform one; and reasonable accuracy for practical purposes is insured. Results, however, are still not so reliably accurate as by combustion, for the reason that even in the same kind of steels the proportion of hardening carbon (which gives no color in the color test) to carbide carbon is not always the same. Fifty consecutive heats of high-carbon open-hearth steel, tested in the manner above described, and also by combustion, showed forty-eight fairly good results by the color method (mostly within 0.03 per cent. of the truth—a few to 0.04 per cent.), and two results (duplicated by both methods) 0.06 per cent. wide of the truth. The standard should be made up of drillings from many different heats mixed together, as was the case here. Crucible steel would show less variation in proportion of hardening to carbide carbon.

GEORGE AUCHY.

NEW BOOKS.

DES INDUSTRIES CHIMIQUES ET PHARMACEUTIQUES. PAR ALBIN HALLER, Membre de l'Institut, Professeur à la Faculté des Sciences de Paris, Rapporteur du Jury de la Classe 87 à l'Exposition Universelle de 1900. Paris: Gauthier-Villars, 1903. 2 vols. quarto. Vol. I, lxxxix + 405 pp. Vol. II, 544 pp. Price, 20 francs.

Perhaps nothing more strikingly illustrates the enormous development of technical chemistry in the last generation than does a comparison of this work of Haller with the famous *Bericht* of A. W. Hofmann, published after the Vienna exposition of 1873. The work of Hofmann was a masterpiece in its way and is still the authority which must be studied in any discussion of the development of chemical manufactures. The number of exhibitors of chemical products at Vienna was not great, but, in discussing the things there shown, opportunity was taken to give a pretty full

¹ If the violent action be prevented at the very start it does not occur at all.

survey of the state of all important chemical industries at the time. Hofmann's *Bericht* is made up really of a series of short monographs by competent authorities.

The work of Haller is also a masterpiece, although in detail it is very different from the book of the Berlin professor. While information is drawn from many sources, the composition appears to be the work of the industrious author alone. At the outset, one is impressed with the great increase of exhibitors in 1900 over 1873, and with the enormous expansion of the industries described.

The Haller report opens with a lengthy general introduction in which is discussed, and very fairly too, the condition of chemical industry in the several countries represented at the exposition. Recognizing the peculiar advanced position occupied by Germany in this field, the author addresses himself to the solution of the question which has attracted so much attention in France, and especially in England in the last ten or fifteen years: Why is the German chemical industry so much in advance of that of other nations? Like the English writers before him, Haller reaches the conclusion that the extraordinary development of the German higher education in the universities and technical schools is the most potent factor in explaining German ascendancy in chemical manufacture. Interesting figures are quoted showing the large sums which have been spent in developing certain of the German laboratories, and on the subject of salaries also something is said which appears surprising to the American reader, who has been so often told that the German professors are very poorly paid for their services.

With respect to the higher chemical education in the United States the remarks of Haller are appreciative and sympathetic. He quotes, at length, from a letter to the *Chemiker Zeitung*, written by Dr. Schneider, at one time professor at the University of Chicago, in which some of our institutions are described in rather dark colors, but explains further that Schneider's picture is somewhat overdrawn. Haller spent some months in this country at the time of the Chicago exposition and wrote a valuable report to his government on his return in which he discussed educational as well as technical matters. He visited several of our larger schools while here, and his observations are of value. "That more is not accomplished with the colossal resources at the disposition of the universities, is the other side of the problem, but each

country must have its own standards, and work things out in its own time." Part of the trouble here, the author very truly says, is found in the condition of our secondary education.

In this introduction, finally, fourteen pages are devoted to the topic "Instruction in Chemistry in France." This will be found instructive reading, since the author has had himself much to do with the awakening now discernible in his country. Throughout there is a comparison with German conditions and methods which cannot fail to incite his countrymen to greater efforts.

The body of the work is made up of ten chapters dealing with different lines of chemical industry. The first and longest of these is devoted to the so-called heavy chemicals, the common acids, alkalies, bleaching-powder, phosphates, nitrates, Stassfurt salts, etc., while the following chapters deal with special fields of work—colors, varnishes, soaps, medicinal chemicals, crude colonial products and so on. Everything from artificial silk to the ozone purification of water seems to be considered, and the discussion is not confined to things exhibited at Paris, but is made complete with much matter drawn from other sources. The author discusses very satisfactorily the great advances which have been made in most of the important chemical industries in the ten years following the earlier French exposition of 1889, and gives for reference numerous bibliographical tables, by the aid of which further information may be obtained. Unusually full statistical information is given regarding such great enterprises as the "Badische Anilin und Soda Fabrik," the "Farbenfabriken vorm. Friedrich Bayer und Co.," the "Farbwerke vorm. Meister, Lucius und Brüning," and others.

Apparently but few chemical exhibits were sent from the United States and some of these were not to our credit or in any way a proper measure of our industry. Haller calls attention to the last and explains that in many directions chemical manufacturers have made colossal advances in this country, that indeed in some important lines we are becoming exporters instead of importers. The development of the electrochemical industries is especially mentioned.

J. H. LONG.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

NOTES ON THE HYDROLYSIS OF STARCH BY ACIDS.

BY GEO. W. ROLFE AND H. W. GEROMANOS.

Received August 5, 1903.

SOME years ago, 1896, Rolfe and Defren¹ published analytical data of acid-hydrolyzed starch products from which they concluded that the evidence was strong that a constant relation existed between the optical rotation and copper reduction of such products, independent of the conditions of hydrolysis; in other words, that hydrolyzed products of the same rotation had the same reducing power, and consequently were identical in composition, providing, of course, that they were normal, unmixed products of acid hydrolysis. Obviously, absolute confirmation of such a far-reaching law could only be arrived at by elaborate and lengthy research.

In 1897, Brown and Morris² published the results of some 500 analyses of *diastase*-converted starch products, showing, in confirmation of their earlier conclusions, that a law of relation did exist, not only in such products themselves, but in their fractions obtained by alcohol.

Perhaps the most important paper, bearing directly on the acid hydrolysis of starch, is that of Johnson, which appeared in 1898.³

¹ This Journal, 18, 869; revised: *Tech. Quart.*, 10, 133.

² *J. Chem. Soc.*, 71, 115.

³ *Ibid.*, 73, 490.

Johnson found a constant relation between optical rotation and cupric reduction, but obtained results at variance with those of Rolfe and Defren.

Johnson concluded that maltose, or its molecular combinations, was not found in acid-hydrolyzed products, but that these bodies could be considered to be combinations of dextrose and a non-reducing dextrin, thus agreeing with earlier work, notably that of Salomon¹ and Pellet,² who had already come to the same conclusion.

Johnson ascribes the differences shown in Rolfe and Defren's data to errors introduced into the work of the latter through lime salts formed in neutralizing the acidified solutions. He publishes but little of his experimental data or the details of his work, but states that he has followed the analytical procedure of Brown and Morris, and that his conversions were made on a water-bath in open beakers. Apparently the hydrolyzing acid was sulphuric, originally, of about half-normal strength. We understand that Krieger has also published a paper confirming the work of Johnson, but we have not been able to find reference to it.

Morris³ stated that the results of his investigations were quite at variance with those of Johnson; that his data indicated the presence of maltose, which he proved to exist in the solutions by obtaining crystals of undoubted maltosazone; furthermore, his results confirmed those of Rolfe and Defren, although he was inclined to doubt the universal application of their law of relation to all acid-hydrolyzed starch products. The untimely death of this brilliant investigator has doubtless prevented publication of his complete work.

Many circumstances have prevented the resumption of these investigations in this laboratory. Only quite recently has this research been taken up again with the following objects: (1) To obtain more data on the "law of relation"; (2) to see whether this law applied to alcoholic fractions; (3) to find out proofs of the existence of maltose in acid-hydrolyzed starch products.

The methods of the English chemists, adopted by us, have been much criticized, owing to the use of an arbitrary specific gravity factor in the calculations. As the use of this factor, its influence

¹ *J. prakt. Chem.* (2), 28, 82.

² *Compt. Rend.*, 2, 450.

³ *Proc. Brit. Assoc.*, Sept., 1899.

on the results, and their relation to the absolute values, etc., have been fully explained by Brown and Morris,¹ it is not necessary to discuss it in detail here. In the present work we have expressed the results in absolute values. It should be noted, however, that the use of the factor 0.00386, as detailed by Brown and Morris, simplifies the calculations, gives correct *proportional* values (per cents.) of the primary carbohydrates, and likewise optical and reducing figures, readily convertible into absolute values by use of known factors. The practical starch chemist, therefore, will probably continue the use of it, as a path of least resistance in attaining his desired information, just as the analyst will use the Mohr cubic centimeter, and the physical chemist the Briggs logarithm instead of the Naperian, when by such means he arrives at his objective point more quickly and easily. Results obtained by such expedients of calculation and experiment are permanently valuable, as they admit of standardization at will in terms of the accepted scientific constants of the day.

Analytical Methods.—In the earlier work, densities were obtained by a Westphal balance, carefully and frequently adjusted, and were made at ordinary laboratory temperatures, and corrected for 15.5°. More recently, we have made pycnometer determinations at 15.5°. Corrections were made for the dissolved mineral salts present. Ash determinations of carbohydrate solutions containing known amounts of mineral salts confirmed O'Sullivan's factor, 0.008, for the density correction of each gram of mineral matter, determined as ash, in 100 cc. of solution, when the amount of mineral matter did not exceed a few per cent. of the carbohydrate present. A more exact correction seems necessary when the mineral content is large. Ash determinations were made in a "low temperature" muffle, vaseline being used to prevent excessive swelling of the coal.

This influence of the mineral salts in solution was investigated with particular care, owing to its possible importance as a source of error, as suggested by Johnson. Evidently the most important error introduced, that of the density, lowers the cupric-reducing power and optical rotation by the same percentage, the error in reduction appearing greater in the higher converted products, that of the rotation in the lower. Hence, the effect of the ash correction on the reduction values of those products containing

¹ *J. Chem. Soc.*, 71, 72.

the most sugars would be diametrically opposite to that suggested by Johnson's criticism. As a matter of fact, the correction for the concentration of acid used rarely exceeds 2 per cent., and in the majority of cases is much smaller. This would tend to increase the discrepancy of more than 10 per cent. between Johnson's and Rolfe and Defren's figures in those products where the presence of maltose is in dispute; that is, at the conversion point where maltose is supposed to be present in maximum amount.

We have made a careful study also of the original data of this earlier work and have recalculated all the results where the data admitted. This was made necessary from the revision of factors used in calculation. We have tabulated all these values figured in absolute constants. It will be seen that little change is made, many of the corrections being compensatory.

Another possible source of error caused by lime salts might be their precipitation with the copper oxide in the Fehling test. This seemed improbable, as the mineral matter rarely exceeded 0.100 gram in 100 cc. in the original solutions, which were diluted in most cases to $\frac{1}{80}$ of their original concentration. Blank tests made on solutions containing lime salts in the proportion present in the usual tests, and in fact, made by neutralizing an acidified solution in the same manner as the hydrolyzed products, showed no increase in weight due to precipitated lime.

The optical rotation constants have been determined by a Schmidt and Haensch saccharimeter, but the light factor used in converting readings to angular degrees of rotation of the "D" ray has been increased 0.2 per cent. to 0.3450. The original factor, 0.3443, which was worked out experimentally,¹ expresses the value of our saccharimeter in terms of yellow-light rotation, measured on a Laurent polariscope, the light being that of a sodium chloride flame, filtered through a section of potassium bichromate crystal. The Landolt polariscope uses sodium chloride, light filtered through a potassium bichromate solution, and also one of uranium sulphate. This seems to have caused a change in light standard which results in readings which are 0.2 per cent. higher. The wave length of the Landolt illuminating apparatus has been found to be 0.00058932,² corresponding to a position in the spectrum exactly midway between the two "D" lines. As the

¹ This Journal, 18, 873.

² Landolt's "Das Optische Drehungsvermögen," p. 264.

Landolt values seem to be generally accepted as the standard for the "D" ray, we have made this trifling change in our own figures. The subject of the "light factor," that is, the equivalent value of one saccharimetric division in angular degrees of yellow-light rotation, is treated by recent text-books in a misleading way. Values are given some tenths of a per cent. higher than those of the earlier works, leading the reader to infer that the earlier figures are incorrect, whereas, as a matter of fact, these earlier factors are practically exact for by far the majority of saccharimeters in actual use to-day—those graduated in "Mohr" cubic centimeters at 17.5° , the only correction being for any change in the light standard of the rather indefinite "D" ray. The recent factors are obviously applicable only to those instruments recently made which are graduated for solutions made up in true cubic centimeters. Unquestionably, the use of volumetric apparatus graduated in true cubic centimeters is most commendable, but just as unquestionably, the starch chemist must use those factors which are applicable to the actual graduation of his saccharimeter. It is to be hoped that the makers of saccharimeters henceforth will mark on the instruments just how they are graduated.

As far as possible, saccharimeter readings have been made at 20° C., but, with the present laboratory facilities at our command, it has been impossible to control the temperature within several degrees. As soon as it is feasible to carry out such work, we intend to make a correction table for readings taken at temperatures other than 20° . Our determinations of cupric-reducing power have been made by Defren's method,¹ with slight modification. We have preferred this method to that of Brown and Morris,² which it closely resembles, merely because we obviate the correction due to the spontaneous reduction of the solution. In the past six years we have made blank tests on every lot of Fehling solution used, carrying out every detail of the regular determination. With the exception of two lots of solution—in which we traced the spontaneous reduction of 0.0017 gram to a bottle of Rochelle salts of inferior quality—we have never found either visible evidence of spontaneous reduction, or increase in weight of crucibles, these checking within 0.0002 gram. Therefore, we state with confidence that there is no spontaneous reduction of

¹ This Journal, 18, 749.

² J. Chem. Soc., (London), 71, 94.

the Fehling solution during the heating process of the test carried out by Defren's method. This seems to be the result of the greater dilution of the Fehling solution, and possibly the smaller amount of alkali. We have varied the method, however, in one detail. Instead of delivering the sugar solution as quickly as possible from a burette into the Erlenmeyer flask containing the hot, diluted Fehling solution, we have added the sugar all at once, without removing the Fehling liquor from the bath, by quickly inverting a 25 cc. flask which is left upside down in the mouth of the Erlenmeyer during the reduction. One short rotary shake is given the Erlenmeyer immediately after the solution is added to insure, at once, perfect mixture. This modification has increased the reducing power of the sugar solutions, and necessitated calculating a new set of equivalents, from tests made with pure dextrose. As we hope to modify the process somewhat more in the near future, we do not deem it advisable to take valuable space to publish our present equivalent table. The copper reduction, in general, both on dextrose and maltose, is about 5 per cent. greater than Defren's original figures, the dextrose equivalent, therefore, being correspondingly less. In the earlier work some correction has been necessary, owing to the more accurate density values for dextrose and maltose, which are now known.¹ These density corrections lower Defren's original equivalents about 0.6 per cent. and need only be considered in the most accurate work.

As the density factors corresponding to the actual weights of acid-hydrolyzed starch products, in solutions of a density approximating 1.04, have already been established experimentally,² we have been enabled to convert our results into absolute values by the following table (A), which gives the logarithms for convert-

TABLE A.—DENSITY FACTORS FOR REFERENCE TO ACTUAL WEIGHTS OF ACID-HYDROLYZED STARCH PRODUCTS IN 100 TRUE CUBIC CENTIMETERS OF SOLUTIONS.

$[\alpha]_{20}^D$	Density factors $\left(\frac{d_{15.5^\circ}^{15.5^\circ}}{15.5^\circ} \right)$	Logarithms of conversion factors. ³
55°	0.003837	9.9965
60°	0.003844	9.9973
65°	0.003850	9.9980
70°	0.003857	9.9988
75°	0.003864	9.9996
80°	0.003870	0.0002

¹ *J. Chem. Soc. (London)*, 71, 79.

² *This Journal*, 19, 698.

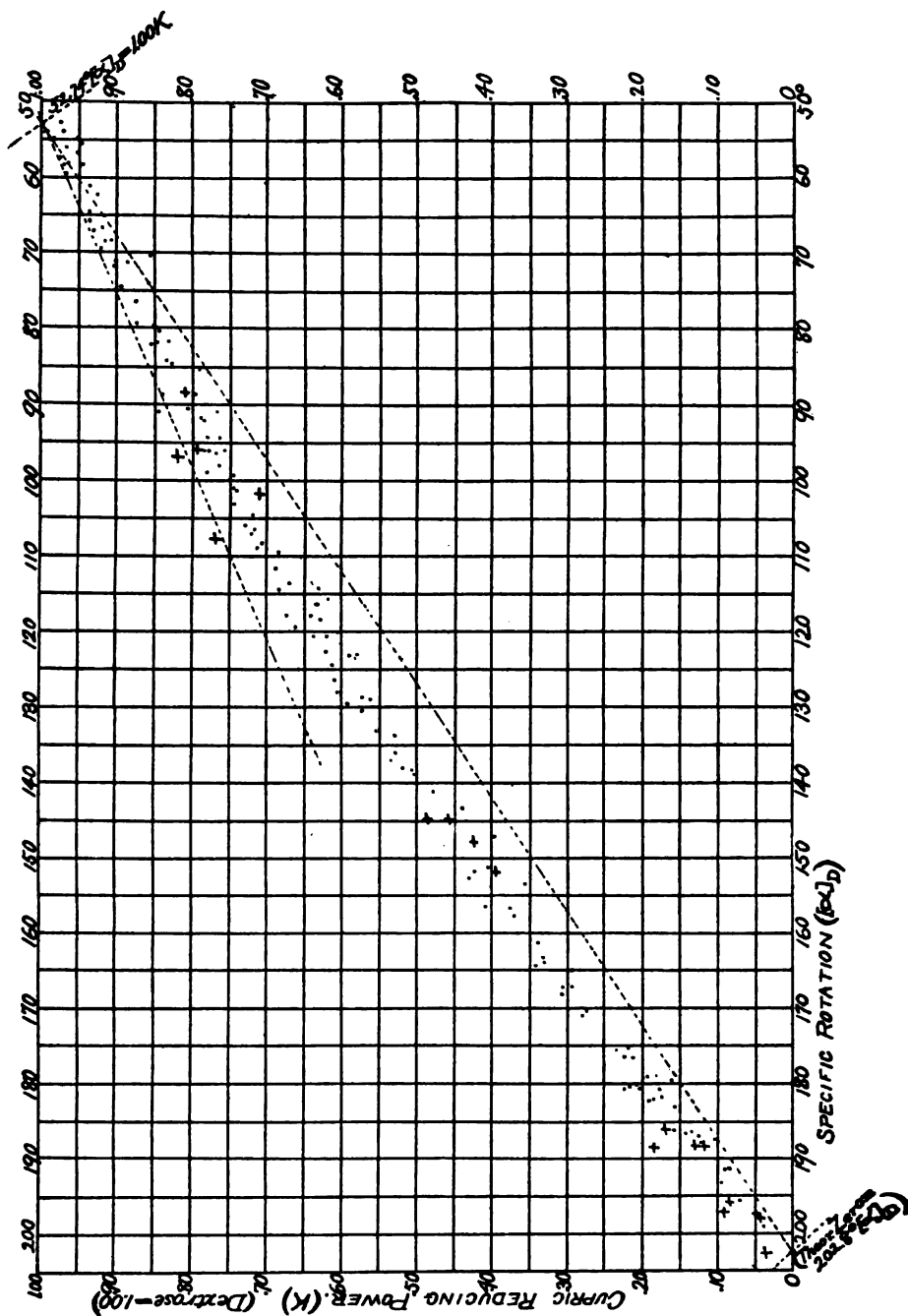
³ $\text{Log. } \frac{F}{0.00386} = 0.00802$.

$[\alpha]_{20}^D$	Density factors $\left(\frac{d_{15.50}^{15.50}}{15.50}\right)$	Logarithms of conversion factors. ¹
85°	0.003877	0.0010
90°	0.003884	0.0018
95°	0.003890	0.0024
100°	0.003897	0.0032
105°	0.003904	0.0040
110°	0.003911	0.0048
115°	0.003918	0.0056
120°	0.003925	0.0063
125°	0.003931	0.0070
130°	0.003938	0.0078
135°	0.003945	0.0085
140°	0.003951	0.0092
145°	0.003958	0.0100
150°	0.003965	0.0107
155°	0.003971	0.0114
160°	0.003978	0.0121
165°	0.003985	0.0129
170°	0.003991	0.0136
175°	0.003998	0.0144
180°	0.004005	0.0151
185°	0.004011	0.0157
190°	0.004017	0.0164
195°	0.004023	0.0170

NOTE.—As the cupric-reducing power of pure dextrose, taken as 1.00 for the factor 0.00386 is 0.9915 in absolute value, it is necessary to add the co-logarithm of this number, or 0.0037, to the logarithm of the conversion factor in calculating the reducing power in terms of that of the equivalent weight of dextrose as unity.

ing results calculated by the factor, 386, into values referred to grams of hydrolyzed product in 100 true cubic centimeters of solution. The newer work published in this paper covers a comparatively limited field, being an investigation of hydrolyzed products of several commercial starches of different origin, formed by the action of hydrochloric acid at two concentrations, and at pressures between 2 and 3 atmospheres, unless otherwise stated. No attempt has been made to purify these starches, as we have been led to believe not only that purification is unnecessary, but may actually change the nature of the starch, since, in our experience, all purification methods produce a certain amount of hydrolytic change and formation of products which are diffusible through the starch grains, and subsequently removed by washing. That

¹ Log. $\frac{F}{0.00386} = 0.99802$



such diffusion actually does take place, can be proved by testing the wash-waters used in the purification of starch with iodine, or shaking up the starch itself with cold water and testing the water. The colors obtained are not the deep blue of the unchanged and indiffusible starch, but the violet of hydrolyzed starch, providing, of course, that the grains are unruptured. Probably this slight loss from hydrolytic change has no influence on the results, when the purification method is not too drastic, but it is questionable whether the "purified" product obtained is any nearer pure *starch* than the original.

The following table (B) gives the corrected values of Rolfe and Defren's original work, together with those recently obtained by us. The plotted results¹ make it clear that the reducing values do not lie on a straight line as they should, if dextrose alone were present. On the contrary, the results are in substantial agree-

TABLE B.

Starch. Corn	Acid. HCl	Concentration. N/100	$[\alpha]_D$	κ .
			147.6	0.489
			100.9	0.750
			73.8	0.855
			199.2	0.043
			179.6	0.161
			156.6	0.375
			129.2	0.563
			149.2	0.451
			88.8	0.799
			65.6	0.937
			58.2	0.974
			53.6	0.977
			180.5	0.206
			133.4	0.555
			108.7	0.712
			68.1	0.921
			59.0	0.949
			151.4	0.403
			118.0	6.637
			90.8	0.768
			70.3	0.855
			61.8	0.933
			164.4	0.346
			135.9	0.529
			92.4	0.786
			168.5	0.305

¹ The plotted values marked by a cross are those of alcoholic fractions, to be discussed in a subsequent paper.

Starch.	Acid.	Concentration.	$[\alpha]_D$	α .
			141.7	0.510
			126.3	0.610
			101.2	0.745
Corn	HCl	N/200	195.6	0.067
			186.3	0.143
			180.6	0.225
			167.3	0.306
			160.3	0.349
Corn	HCl	N/100	108.1	0.705
			94.4	0.778
			81.9	0.854
			76.3	0.877
			187.7	0.122
			159.9	0.382
			120.5	0.640
			74.5	0.899
			71.1	0.902
Corn	H ₂ C ₄ O ₄	N/100	181.8	0.172
			160.1	0.360
			138.7	0.504
Corn	H ₂ C ₄ O ₄	N/50	140.9	0.485
			134.0	0.529
			120.4	0.623
			58.1	0.970
			136.9	0.538
			87.1	0.896
Corn	HCl	N/100	182.3	0.192
			186.9	0.128
			193.3	0.097
			186.0	0.158
			182.0	0.186
			180.3	0.217
			167.2	0.298
Potato	HCl	N/50	164.9	0.296
			153.9	0.358
			143.5	0.444
			144.9	0.457
			137.6	0.523
			127.8	0.604
			119.6	0.660
			163.9	0.333
			124.6	0.614
			116.2	0.639
			111.5	0.694
			103.2	0.750
Corn	HCl	N/50	130.4	0.574
			125.5	0.617

HYDROLYSIS OF STARCH BY ACIDS.

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Starch.	Acid.	Concentration.	$[\alpha]_D$.	n .
Corn	HCl	N/50	117.7	0.645
			114.2	0.673
			107.3	0.723
			109.7	0.680
			104.7	0.722
			99.3	0.750
			95.9	0.760
Cassava	HCl	N/50	91.9	0.790
			90.4	0.808
			79.8	0.852
			78.6	0.875
			74.0	0.884
			71.7	0.903
			96.2	0.773
"Thin boiling" corn-starch	HCl	N/50	90.6	0.850
			84.3	0.835
			81.8	0.851
			66.7	0.933
			60.8	0.941
			59.5	0.973
			57.5	0.980
			122.5	0.623
			114.6	0.631
			106.5	0.720
			97.6	0.769
Corn	HCl	N/50	179.2	0.195
			52.5	100.4
			68.1	0.910
			59.9	0.977
Corn	$H_2C_2O_4$	N/25	56.7	0.953
			163.6	0.333
			129.0	0.569
			98.9	0.783
Corn	H_2SO_4	N/50	80.1	0.849
			69.3	0.925
			170.9	0.281
			130.0	0.562
			105.9	0.728
Corn	HCl	N/100	84.8	0.832
			71.3	0.889
			152.6	0.427
			95.7	0.788
			66.5	0.924
Corn	HCl	N/50	54.8	0.954
			54.2	0.998
			95.8	0.783
			64.6	0.939

Starch.	Acid.	Concentration.	$[\alpha]_D$.	κ .
			55.5	0.972
			52.9	0.979
			88.7	0.843
			55.3	0.951
Corn	HCl	N/25	157.5	0.372
			114.7	0.686
Corn	HCl	N/50	82.0	0.886
			54.9	0.993
Potato	HCl	N/50	175.5	0.234
			151.3	0.404
			180.1	0.208
			156.6	0.406
			191.3	0.094
			176.8	0.213
			158.8	0.331
			123.2	0.592
			123.0	0.583
Cassava	HCl	N/50	151.6	0.427
			182.2	0.184
			118.5	0.668
			183.4	0.157
			94.6	0.783
			85.1	0.795
Potato	HCl	N/50	187.3	0.104
			175.3	0.220
			161.1	0.340
			191.2	0.087
			186.1	0.135
			180.7	0.176
			176.7	0.221
			170.4	0.275

ment with the original ones of Rolfe and Defren. While the tabulated values of the original paper, calculated on the factor 0.00386, are not exact, they have proved to be sufficiently approximate to be valuable aids in predicting practical laboratory results. It is intended to use more refined methods of analysis, if possible, and to locate this curve more definitely by the method of least squares. We have published the present figures, however, as conclusive of the presence of another reducing body than dextrose in acid-hydrolyzed starch products, formed under the conditions of conversion which we have defined.

THE PRESENCE OF MALTOSE IN ACID-HYDROLYZED STARCH PRODUCTS.

BY GEO. W. ROLFE AND ISAAC T. HADDOCK.

Received August 5, 1903.

REFERENCES have already been made, in a previous paper,¹ to the works of Salomon, Pellet, Johnson, and others which have led these investigators to conclude that maltose is not a product of the acid hydrolysis of starch. Lintner and Dull believed that "isomaltos" was produced. Morris and Rolfe and Defren have been among those who have maintained that maltose resulted from the hydrolysis. As has already been cited in a previous paper, Morris has stated that he has made crystals of undoubted maltosazone from the products of acid-hydrolyzed starch.

Having at hand a large quantity of commercial "glucose," of which we knew the circumstances of manufacture—it being the product of hydrochloric acid hydrolysis at a pressure of two atmospheres, and having a specific rotation of 126.5° D, and a cupric-reducing power of 0.575—we decided to make alcoholic fractions of this glucose with the object of separating maltose, if present, or some of its compounds, and, incidentally, of testing the law of relation of rotation to cupric reduction as applied to alcoholic fractions. The analytical figures of this sample showed that the hydrolysis had been carried only a little beyond the point for maximum maltose content as calculated from Rolfe and Defren's tables, and, in consequence, was specially suited for the investigation.

It can be easily calculated from the same tables that, were it possible to remove all the dextrin from a solution of this glucose leaving all of the maltose and dextrose, the resulting product would have a rotation of 105° and a reducing power of 0.76. If, however, the fractionation separated the glucose into a series of products more or less soluble in alcohol, but containing all three of the primary carbohydrates, it would be probable that they would conform to the law of relation, in which case, should a product be separated of the rotation 105° , its cupric-reducing power would be about 0.71 instead of 0.76.

In carrying out the fractioning, a 15 per cent. solution of glu-

¹ Preceding paper.

² *Ber. d. chem. Ges.*, 28, 1522.

cose was added, drop by drop, to about ten times its volume of 95 per cent. alcohol. After standing for a day or more, the precipitate was filtered off, washed thoroughly with alcohol, dried at a gentle heat till all traces of alcohol were expelled, and tested in the usual way. In the case of the alcoholic filtrates, the alcohol was removed by distillation, and the residues were concentrated to about 10 per cent. In order to economize time and alcohol, a little fuller's earth was mixed with the first precipitates to facilitate separation.

The following table gives the optical and reducing constants of those fractions which were investigated. It will be seen that, in general, they show a relationship between optical rotation and copper-reducing values which is in practical agreement with that found for homogenous acid-hydrolyzed products.

ALCOHOLIC FRACTIONS OF COMMERCIAL GLUCOSE SOLUTIONS.

<i>1st.</i>	<i>Fractionation:</i>	$[\alpha]_D$	<i>n.</i>
	1st. Precipitate	145.2°	0.489
	2nd. "	149.0°	0.423
	3rd. "	198.0°	0.047
	4th. "	197.6°	0.051
	1st. Filtrate	107.9°	0.765
	2nd. "	101.6°	0.717
	3rd. "	98.3°
	4th. "	96.8°	0.815
<i>2nd.</i>	<i>Fractionation:</i>		
	2nd. Precipitate	188.0°	0.117
	3rd. "	197.2°	0.093
	4th. "	196.0°	0.085
	2nd. Filtrate	88.8°
	4th. "	88.1°	0.811
<i>3rd.</i>	<i>Fractionation:</i>		
	1st. Precipitate	154.6°
	2nd. "	168.1°
	3rd. "	185.7°	0.163
	2nd. Filtrate	84.4°
<i>4th.</i>	<i>Fractionation:</i>		
	1st. Precipitate	137.5°
	2nd. "	152.3°	0.395
	3rd. "	165.9°
	4th. "	187.9°	0.127
	5th. "	189.1°	0.189
	6th. "	194.3°	0.075
	1st. Filtrate	96.0°	0.792

The values for the cupric-reducing powers of the filtrates of the first fractionation all show a wide departure from such relationship. These filtrates were peculiar in that they deposited, to some extent, granular precipitates quite different in appearance from the separated dextrans. It seemed probable that this precipitate was sugar in a free state. Moreover, it seems more than a coincidence accounted for by experimental error that the plots of these reducing values almost exactly fall on a straight line joining the 100 and 62.2 points which theoretically defines the reducing values of mixtures of pure maltose and dextrose. The apparently low reducing power of the second filtrate may be caused by an error in the rotation reading, as the aqueous solution in this case was turbid. This evidence seems to point to the possibility that under certain conditions, not clearly defined, alcoholic fractionation may break up the hydrolytic products, setting free one or more of the primary carbohydrates.

Some of the precipitates, especially those of high rotation, show unexpectedly high cupric-reducing powers. We are inclined to believe that this is caused by partial hydrolysis during drying. The precaution of drying in a vacuum at low temperature may not have prevented this entirely, as these low-converted dextrans seem very sensitive in this respect.

An aqueous solution made from the second filtrate of the third fractionation was heated on a water-bath with a small quantity of a solution of phenylhydrazine, in glacial acetic acid. Maltosazone was separated in the usual way by filtering off the dextrosazone in a hot funnel. On cooling the filtrate, characteristic crystals of maltosazone separated out. The dried crystals, tested by heating in a capillary tube, attached to a thermometer bulb, and immersed in a sulphuric acid bath, according to the usual method, began to decompose at about 195°, being entirely melted at 203°. The ordinary basic lead acetate solution of a density of 1.25, such as is commonly used in sugar analysis, proved very convenient for separating maltose. This solution was not precipitated when dropped into pure 95 per cent. alcohol, but formed a white, curdy precipitate when poured into the alcoholic filtrate from the glucose fractionation. After the lead was completely removed by hydrogen sulphide, the aqueous solution was heated with phenylhydrazine. No precipitate formed in the hot solution,

but maltosazone separated out on cooling. As this seems a promising means of separating maltose, we intend to investigate it further.

We have made some photo-microscopic studies of the maltosazone and dextrosazone obtained from the alcoholic fractions and by means of the lead acetate separation, comparing them with corresponding osazones obtained from pure maltose and dextrose. When pure maltose is treated with phenylhydrazine acetate in the usual way, the osazone often separates out in crystal plates large enough to be seen without magnification. If examined under the microscope, it will be noticed that these plates tend to collect in spherical masses. Plate I shows such crystals of the osazone made from Kahlbaum's C. P. maltose. We have found it impossible to obtain these large crystals by recrystallization from hot water, the osazone being deposited in small balls¹ which show, on close examination, that they are aggregates of flat crystals. Plate II, while a poor photograph, is interesting because it represents these balls obtained from the crystals shown in the first plate by recrystallization from hot water. Plate III shows crystals of maltosazone obtained from the alcoholic filtrate previously mentioned. This shows the plates in loose aggregations and in balls. Plate IV is of osazone crystals from the lead acetate precipitate of the same filtrate. Plate V shows the same crystals after the aggregates have been broken up by gentle tapping of the cover-glass.

Dextrosazone has a quite different crystal habit. The crystals can be described as needles rather than plates. They form brush-like bundles resembling tufts of broom-corn, which, to some degree, suggest the maltosazone aggregations, but yet are quite different, showing none of the compact, spherical forms so characteristic of maltosazone. More highly magnified dextrosazone crystals closely resemble in shape those of stibnite, and apparently belong to the orthorhombic or hexagonal system. Plate VI shows these characteristics, especially the square basal angles. We have found these crystal forms so characteristic, when studied with the microscope, that we have felt warranted in presenting these photo-micrographs, and would have illustrated further the osazones of these two sugars had space permitted. The crystal-line structure and the behavior of the two osazones with hot water

¹ Grimbert: *J. Pharm. Chim.*, 7-17-5, aptly terms them "rosettes."



Plate I.

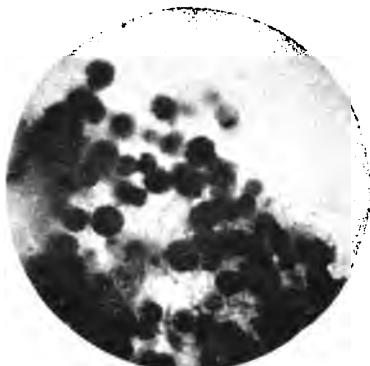


Plate II.



Plate III.



Plate IV.



Plate V.

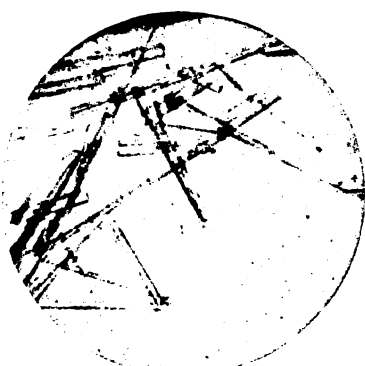


Plate VI.



are, in our opinion, their most easily recognized distinctions. The melting-point test by itself, as already pointed out by Brown, Morris and Miller,¹ is unreliable, and has led to serious errors of identification. This is due to the slight differences in the values in the case of many of the sugars, the difficulty in getting the exact melting-points owing to decomposition, and the great influence of very small amounts of impurities difficult to remove.

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A STUDY IN RAFFINOSE DETERMINATIONS.

BY DAVID L. DAVOLL, JR.

Received July 23, 1903.

THE existence of several methods for the determination of raffinose in the presence of saccharose, together with variable results obtained in the application of the same to the analysis of the same product, have impelled me to investigate the matter more closely after the close of the "campaign." As the result of a study of the various methods, I have been led to combine the best features of some of them and believe that I have succeeded in applying a slight modification to the method of Clerget, which will secure for it accurate and satisfactory results with dark-colored products. The modification proposed is that of applying powdered zinc after inversion and at the temperature of inversion, with the production of an almost colorless solution with no change in the products of the hydrolysis of either sucrose or raffinose.

As the basis of these experiments a pure, doubly refined, white sugar, of undoubted cane origin, was employed and a commercial sample of raffinose from the house of Kahlbaum. The cane-sugar was perfectly free from invert-sugar and polarized 99.97 per cent. pure after being powdered and dried at a temperature of 60°-70° C.

The one sample of molasses was employed throughout the work.

Three samples of animal charcoal were purchased from a reliable Chicago firm and in original packages as bottled by the German firms of Merck and Dr. König. These chars were dried to constant weight before use at a temperature between 115° and

¹ *J. Chem. Soc. (London)*, 67, 709: "The Isomaltose of C. J. Lintner."

125° C. It is important to know that the moisture content of these chars varied from 7.17 per cent. to 25.7 per cent.

The modern double-field S. and H. instrument employed was very recently checked by means of a quartz plate kindly loaned by the Division of Chemistry, U. S. Dept. of Agriculture, Washington, D. C., and all important points on the scale verified by a pure sugar standardized against the quartz of 90 per cent. polarization. The levo-rotation, when checked against the dextro-rotation, gave the same figure in every instance. The flasks used were all restandardized to hold 100 Mohr cc. All polarizations, both direct and invert, were made in the same jacketed 200 mm. tube and at the standard temperatures of 17.5° C. (for direct) and 20° C. (for inverted) so as to avoid all corrections for variation in specific rotation. The readings as given are averages of at least five separate rereadings.

Some work by G. Reinhardt,¹ calling attention to the often increased levo-rotation where char is used for decolorizing "rest" molasses arising from strontium juices, has impelled me to apply the samples of char mentioned for the purpose of reviewing his findings. Reinhardt mentions that bone-black has been regarded, up to the present time, as diminishing levo-rotation by absorption, while blood-char, in spite of its superior decolorizing power, had to be given up because of high absorption.

Following are our results in determining the effect of char upon a solution of pure cane-sugar after hydrolysis by the strict method of Clerget.

	Original polarization.	Calculated normal basis.
(1) Carbo Sanguinis, acido depur. pro analyse. Dr. König.....	—16.41	—32.82
(2) Animal charcoal, Merck, highest purity, dry	—16.29	—32.58
(3) Animal charcoal, Merck, reagent.	—16.21	—32.42

I have not found the levo-rotation diminished by Carbo Sanguinis, but rather slightly increased. Three grams of all chars were used and the vigorous shaking continued five minutes, with three minutes allowed for filtration. Reinhardt found slight diminution, increasing with blood char.

¹ G. Reinhardt, 1902: "Ueber Raffinosebestimmungen," *Ztschr. d. Ver. f. d. Röhrenzuckerind. d. deutsch. Reiches*, 2, 114.

Dr. G. Wiske has elaborated Reinhardt's investigation, working also with dextrose, levulose and galactose in their separate behavior toward chars. Differing with Reinhardt, he finds absolutely no absorption or change when char is applied five minutes to inverted pure sucrose. He explains this invariability by showing in a test with equivalent quantities of levulose and dextrose that the notable absorption of dextrose, together with small absorption of levulose, mutually counteract any error. Where raffinose is present the results are different.

Reinhardt has shown that with rising raffinose content there is increased levo-rotation. In the case of bright after-products having 2.5 per cent. raffinose and using 3 grams of "Klaerkohle" he found the same levo-rotation. He explains this by saying that the absorptive power which diminishes the levo-rotation in the case of inverted pure saccharose is compensated by the simultaneous increase in levo-rotation of inverted raffinose; also due to absorption; hence, where 2.5 per cent. raffinose is present the results are correct, while with less than 2.5 per cent. too little saccharose and too much raffinose is found, though the error is small, while with more than 2.5 per cent. raffinose, too much saccharose and too little raffinose is found. Reinhardt further considers that high levo-rotation is due to absorption of dextro-rotatory melibiose, but he awaits further investigation.

Wiske has also imitated a mixture of raffinose and saccharose by inverting and polarizing a mixture of saccharose, levulose and melibiose, finding a very strong increase in levo-rotation with use of char. In experiments upon mixtures of saccharose and raffinose as they occur in after-product massecuites, sugars and "rest" molasses, he finds the degree of absorption to be entirely dependent upon the quantity of raffinose and indifferent to the quantity of saccharose. Employing half-normal and 3 grams char, he recommends a subtractive correction of $1/10$ degree for every per cent. of raffinose above 2 per cent.

To ascertain the comparative effect of the three varieties of char upon hydrolyzed mixtures of pure cane-sugar and raffinose, 12.367 grams cane-sugar and 0.657 gram raffinose were hydrolyzed in 75 cc. dilution, according to the strict Clerget method, shaking five minutes with 3 grams char and filtering two to three

¹ G. Wiske, 1902: "Ueber Raffinosebestimmungen," *Ztschr. d. Ver. f. d. Rubensucker- und d. deutschen Reiches*.

minutes. The direct polarization of a normal solution of such a mixture was 102.48 per cent.

	Original polarization.	Calculated normal.	Raffi- nose.	Sucrose.
Polarization without char.....	-13.50	-27.00	4.16	94.77
(1) Carbo Sanguinis, acido depur. pro analyse. Dr. König	-13.57	-27.14	4.11	94.87
(2) Animal charcoal, Merck, highest purity, dry	-13.70	-27.40	3.95	95.16
(3) Animal charcoal, Merck, reagent	-14.00	-28.00	3.56	95.89

The samples of blood-char, under the conditions, produced a levo-rotation that results in a raffinose content not far removed from polarization without char, which may be explained by the absorption of dextro- and levo-rotatory substances, mutually offsetting each other.

A notable increase in levo-rotation will be shown later in further comparative tests.

The effect of time as a factor in decolorizing, is shown where Merck's highest purity char is used upon the molasses:

	Time of char digestion. Minutes.	Filtra- tion. Minutes.	Original polarization.	Calculated normal.	Raffinose.	Sucrose.
(1).....	5	7	-5.48	-10.96	3.58	43.97
(2).....	10	9	-5.51	-11.02	3.54	44.04
(3).....	15	9	-5.55	-11.10	3.49	44.13
(4).. Decoloration by zinc			-5.48	-10.96	3.58	43.97

The decoloration after fifteen minutes, while slightly more than that of five minutes, was not worthy of consideration. The result in (4) is that obtained by the action of 1 gram powdered zinc for three to four minutes at 69° C. after completion of inversion by the strict method of Clerget and is the modification I would propose as a solution of the vexatious problem of bleaching. It is added here for the sake of comparison and will be referred to later. The direct polarization of this molasses was 50.6 per cent., using lead -b- acetate as a precipitant, with and without acetic acidulation, producing identical results in polarization.

The method of Lindet as modified by Courtonne was examined, but gave such widely varying results with a mixture of pure cane-sugar and raffinose that the results obtained upon a low product, like molasses, may be credited with difficulty. The method is as follows: 20 cc. of a solution containing $\frac{1}{2}$ normal of the substance is placed in a 50 cc. flask, and 5 grams of zinc dust, accurately weighed, are placed in the flask. Heat the flask and con-

tents by immersing in boiling water. Add 10 cc. of dilute hydrochloric acid in portions of about 2 cc. at a time and as frequently as convenient. Prepare the dilute acid by adding to pure hydrochloric acid (sp. gr. 1.2) an equal volume of distilled water. Heat a few minutes after the last addition of acid. The undecomposed zinc occupies a volume of 0.5 cc.; hence, the normal invert reading is obtained by multiplying by 2.475. After the inversion is completed, cool the solution, either quickly or slowly, by setting aside. Complete the volume at 20° C. Mix, filter and polarize at 20° C.

In his original article, Lindet directs that 5 cc. concentrated hydrochloric acid be gradually added in 4 or 5 parts at intervals of five minutes, and that the zinc be filtered off before dilution to 50 cc. A formula is given for use with the Laurent instrument. Spencer¹ gives a formula for use with the S. and H. instrument as follows:

$$(1) \text{ Sucrose} = \frac{C - 0.493 A}{0.827} \quad (2) \text{ Raffinose} = \frac{A - \text{Sucrose}}{1.85}$$

where A = the direct reading, and C = algebraic sum of direct and invert reading.

For convenience, all calculations based upon formulas (1) and (2) will be designated "Lindet" merely to distinguish them from Herzfeld's.

Results obtained by the Lindet-Courtonne method upon a mixture consisting of 4.9468 grams cane-sugar and 0.2628 gram raffinose (total = $\frac{1}{3}$, normal) in 20 cc. distilled water, were as follows:

Original invert reading.	Result on normal.	Raffinose.		Saccharose.		
		(Lin- det.)	(Herz- feld.)	(Lin- det.)	(Herz- feld.)	
-10.07	-25.18	4.97	5.33	93.28	92.60	2 cc. dilute hydrochloric acid added every four to five minutes and heated five minutes additional; zinc filtered out.
-9.25	-22.89	6.47	6.81	90.51	89.87	The above repeated, but the zinc <i>not</i> filtered out.
-7.00	-17.32	10.05	10.40	83.89	83.23	Whole 10 cc. hydrochloric acid added within three minutes, and heat applied twenty minutes in all; zinc <i>not</i> filtered out.
Result by Clerget method		3.78	4.16	95.48	94.77	(For purpose of comparison.)

¹ Spencer: "Handbook for Chemists of Beet-Sugar Houses and Seed-Culture Farms,"

These results show that the method is totally unreliable with products of the above composition.

The Lindet-Courtonne method was then applied to the molasses having a direct polarization of 50.6 per cent. and which by Clerget's method, using 3 grams char and shaking five minutes, gave 3.58 per cent. raffinose and by the decolorization with 1 gram zinc, as is proposed, also 3.58 per cent. raffinose.

Original invert reading.	Result on normal.	Raffinose.		Saccharose.		
		(Lin- det.)	(Herz- feld.)	(Lin- det.)	(Herz- feld.)	
-4.18	-10.45	3.76	3.91	43.65	43.36	Adding hydrochloric acid every five minutes; total heating, twenty-five minutes; cooling quickly and filtering out zinc.
-4.35	-10.77	3.55	3.70	44.04	43.74	Adding hydrochloric acid every four minutes; total heating, twenty-one minutes; cooling quickly zinc <i>not</i> filtered out.

The inversion even on "rest" molasses varies with varying conditions of time, etc. The results, besides varying beyond limits of error among themselves, vary also from the results obtained by the standard method, as shown above, where chars are compared upon molasses.

Perhaps the most instructive result is that shown in the following experiment, where are compared: (1) The strict Clerget method without char; (2) the strict Clerget method with 3 grams of Merck's highest purity char after five minutes' shaking; (3) the Lindet-Courtonne method, adding 2 cc. hydrochloric acid every four minutes and heating thirty minutes in all; (4) the Herles method, using 10.6 cc. lead nitrate solution and one-half equivalent sodium hydroxide; (5) the proposed modification to the strict Clerget method, *i. e.*, addition of 1 gram powdered zinc. Each 100 cc. of original solution contained 11.4612 grams pure cane-sugar and 0.814 gram raffinose. It was the intention to secure the same polarization as obtains in ordinary "rest" molasses with a content of 2.5 per cent. raffinose. With the exception of the Lindet-Courtonne method, 50 cc. of the original solution were taken for inversion. With the Lindet-Courtonne method, the prescribed 20 cc. were used in a 50 cc. flask and the zinc volume allowed for.

Original invert reading.	Results of normal.	Direct polariza- tion.	Raffinose. (Lin- det.) (Herz- feld.)		Saccharose. (Lin- det.) (Herz- feld.)		
(1) -5.87	-11.74	48.60	...	2.65	43.70	Strict Clerget.
(2) -6.39	-12.78	48.60	...	2.00	44.91	Strict Cler- get with char.
(3) -4.52	-11.19	48.60	2.86	3.01	43.32	43.02	Lindet- Courtonne.
(4) -5.97	-11.94	47.47	...	2.30	43.22	Herles.
(5) -5.86	-11.72	48.60	...	2.67	43.65	Proposed method.

With the strict Clerget method and use of char the increased levo-rotation is very considerable and causes a very notable variation in sucrose and raffinose from the truth. The Lindet-Courtonne method, while not showing such great variation, is still unsatisfactory and does not inspire confidence; furthermore, the writer finds inversion under its conditions more time-consuming than under any other. The modification to Clerget's method that I propose seems to give results concurring with the strict Clerget method, both here and with molasses; also in a later experiment, where the proportion of raffinose is increased.

The method next inquired into is that of Herles,¹ with the object of ascertaining its action where raffinose is present. No comparison was made of it upon inverted pure cane-sugar solutions.

Herles' chief objection to determinations by inversion as carried out up to that time was, that clarification by means of lead acetate for direct polarization and not for invert, would give wrong results, because optically active substances are precipitated in the operation for direct polarization, which remain in the inverted solution and either retain their whole optical activity or the acid changes it, or perhaps the optical activity is for the first time developed during inversion.

Degener has shown that invert sugar by evaporation, even *in vacuo*, loses its theoretical levo-rotation and finally becomes dextro-rotatory, which, by treatment with hydrochloric acid, according to Clerget, soon takes on its original levo-rotation; hence, it affects only the invert reading.

Herles states that lead nitrate remaining in excess as such has only insignificant action, and Herzfeld admits that the action is

¹ Herles, 1890: "Ueber die Bestimmung des Zuckers durch die Inversionsmethode," *Zschr. d. Ver. für d. Rübensuckerind. d. deutsch. Reiches*, p. 217.

small. Herzfeld states that sodium nitrate heightens the polarization and, while admitting that basic lead nitrate is a remarkable decolorizer, affirms that it carries down sugar with it, especially if the alkali be added all at once, and even a little if it be added drop-wise. Neutral salts, with the exception of the acetates, increase the levo-rotation, but the acetates reduce the free hydrochloric acid and thus lower inverting or hydrolyzing power; hence, Herles was led to consider PbOHNO_3 as the most suitable form. He used "a lead nitrate solution of 1.3856 specific gravity (or about saturated), and in which 1 cc. = 0.3102 lead." This could not be correct, since a stronger solution of lead nitrate, *i. e.*, specific gravity 1.414, and containing 35 per cent. lead nitrate only contains the equivalent of 0.3094 gram lead.

He distinctly states that the solution should not be alkaline, as lead saccharate would be precipitated and, while proving that resulting potassium nitrate causes increased levo-rotation, belittles it by adding that the solutions are always weak in sugar where much potassium nitrate is formed.

The solution of lead nitrate used for this experiment had a specific gravity of 1.33233 and contained the equivalent of 0.2488 gram lead or 0.398 gram lead nitrate, equaling 29.872 per cent. Accordingly, 1 cc. of this lead nitrate, to form the stipulated basic salt, will require 1.202 cc. normal sodium hydroxide, or where the standard alkali has a corrective factor of 1.061 as in this instance, 1.133 cc. A normal of molasses was weighed out, and after dilution to about 70 cc. the specified quantities of lead nitrate solution added and then the alkali solution gradually and with rotation of flask, when all was carefully diluted to exactly 100 cc. at 17.5° C. 10.6 cc. lead solution and 12 cc. alkali solution cleared the solution perfectly and left no excess of alkali.

	Pb(NO ₃) ₂ solution. cc.	NaOH solution. cc.	Direct reading.	Invert reading.	Raffinose.	Saccharose.
(1)	9.00	12	50.75	—5.86	3.77	43.77
(2)	10.60	12	51.10	—5.86	3.85	43.98
(3)	12.00	12	50.99	—5.86	3.82	43.92

In samples (2) and (3), considerable lead chloride was thrown down. In such work of Herles as has come under our notice, the absence of very specific directions as to the limits of lead to be used, has left us without much information, and an intimate study

of the best conditions is not warranted, as the process has the serious defects already referred to.

The direct polarization on the same sample varies quite a little from that where lead basic acetate is used (*i. e.*, 50.6 per cent. pol.) which may be accounted for by the action of the lead salt upon the invert sugar present, which is a trifle less than 2 per cent. In the former table, where the five methods are compared, we have shown a reduction from 48.6 to 47.47 per cent. polarization where basic lead nitrate was used; hence, this is probably more than compensated for by the modified levulose rotation. To recapitulate, the results obtained so far by the different methods upon molasses, we have:

	Raffinose.	Saccharose.
Strict Clerget, with char.....	3.58	43.97
Proposed method, adding zinc.....	3.58	43.97
Lindet-Courtonne, varying conditions....	3.91	43.36
with Herzfeld's formula....	3.70	43.74
Herles' method, applied.....	3.85	43.98 $\frac{1}{2}$ equivalent sodium hydroxide.

The next experiment shows (1) the absorbent effect of char upon the products of the hydrolysis of pure saccharose and pure raffinose when they are mixed in varying proportions; also (2) results by the proposed new zinc modification to the strict Clerget method, when compared with the strict Clerget method without the use of char.

Direct reading.	Invert reading without char.	Invert reading with char.	
25.62	-6.62	-7.01	Used 0.3285 gram raffinose and 6.1835 grams sugar.
48.60	-5.87	-6.39	Proposed zinc modification.
48.60	-5.87	
53.40	-4.58	-5.57	Proposed zinc modification.
53.40	-4.57	

17.1917 grams sugar and 1.221 grams raffinose.

17.1917 grams sugar and 2.442 grams raffinose.

The zinc in the presence of the hot hydrochloric acid at 69° C. has, therefore, absolutely no effect upon the products of the hydrolysis of saccharose and raffinose. It has been found advisable to filter out, by means of a very small tuft of cotton, the residue from the 1 gram of zinc left after cooling to 20° C., with quantitative washing, of course, since the continued, slow evolution of hydrogen may disturb proper dilution to the mark.

The author wishes to add some tests made upon the correctness of Herzfeld's formula for the temperature correction for raffinose:

AS APPLIED TO HYDROLYZED HALF-NORMAL CANE-SUGAR IN 100 CC.

Temperature. °C.	DILUTION.	
	Original reading.	Calculated to 20° C. normal inversion.
17.2	—17.06	—32.59
20.0	—16.32	—32.64
20.9	—16.07	—32.59
21.6	—15.93	—32.66

AS APPLIED TO MIXTURE OF 12.367 GRAMS CANE-SUGAR AND 0.657 GRAM
RAFFINOSE IN 100 CC. DILUTION.

Temperature. °C.	DILUTION.	
	Original reading.	Calculated to 20° C. normal inversion.
16.4	—14.40	—27.00
20.0	—13.50	—27.00
23.0	—12.78	—26.97

It is not advisable to make the polarization at any temperature without the use of the jacketed tube.

CARO, MICHIGAN,
April 22, 1903.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, LABORATORY OF IN-
SECTICIDES AND AGRICULTURAL WATERS, U. S. DEPT. OF
AGRICULTURE, No. 52.—SENT BY H. W. WILEY.]

A COMPARATIVE STUDY OF METHODS OF DETERMINING FORMALDEHYDE.

BY BERNARD H. SMITH.

Received June 26, 1903.

THE uses of formaldehyde have widely increased during the past few years. As a disinfectant it has come to be used in enormous quantities by health inspectors, its vapor or a dilute solution destroying many kinds of pathogenic bacteria; as a preservative it is one of the most effective and one of the most convenient to use; it is an important fungicide, the agriculturist finding it a valuable aid in combatting certain plant diseases, while as an insecticide it rids man of those insects, often more plentiful than appreciated, that choose to live in the crevices close to his food or his bed.

With the increasing use of formaldehyde, many new methods have been suggested for its quantitative determination. While some of these are rather difficult of manipulation or have other

drawbacks, others are of great value. With the view of determining, if possible, which of the commonly used methods was the most accurate and which could be applied to strong and which to weak solutions with the greatest convenience, this study was undertaken.

The solutions were made up in large quantities and kept closely stoppered, the same solutions being employed in all the methods tested. The strongest of these was the commercial formalin advertised to contain 40 per cent. formaldehyde. The others contained approximately 15 per cent., 10 per cent., 5 per cent., 1 per cent., $\frac{1}{10}$ per cent., and $\frac{1}{100}$ per cent. It should be stated that the last three were made up quite accurately, while the others contained somewhat less than the percentages given. The methods worked with up to the present time are as follows: The Blank and Finkenbeiner, the Legler, the gravimetric hexamethylenetetramine, the iodimetric, the potassium cyanide and the volumetric aniline method. In the following tables, Roman numerals are used to indicate the solutions, the strongest being I, the second strongest II, and so on to VII.

THE BLANK AND FINKENBEINER METHOD.¹

This method is as follows:

About 3 grams of the formaldehyde solution are weighed into a flask containing 25 cc. of double normal sodium hydroxide. Then 50 cc. of hydrogen peroxide of approximately 3 per cent. strength is added cautiously, the addition lasting three minutes. The hydrogen peroxide oxidizes the formaldehyde to formic acid, which in turn is neutralized by the sodium hydroxide present, as shown in the following equation:



The excess of alkali is titrated with twice normal sulphuric acid, using litmus as indicator.

The following results were obtained:

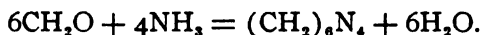
I.	II.	III.	IV.	V.	VI.	VII.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
37.28	14.43	9.74	4.86	1.02
37.27	14.45	9.80	4.81	1.01
37.33	14.48	9.67	4.75	1.05

It is important that a few minutes should elapse after the addition of the hydrogen peroxide for the titration.

¹ *Ber. d. chem. Ges.*, 31, 17, 2979 (1898).

THE LEGLER METHOD.¹

A definite quantity of the formaldehyde solution is placed in a flask containing more normal ammonia than is required for the formation of the corresponding hexamethylenetetramine, which is formed as follows:



After standing, the excess of ammonia is titrated back, using rosolic acid as indicator.

Results were obtained with this method as follows:

I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.	VII. Per cent.
36.99	14.44	9.62	4.55
37.08	14.50	9.72	4.42
37.14	14.40	9.82	4.33

Concordant results were hard to obtain with solutions of less than 5 per cent. in strength, though with the stronger solutions the results were very good. Care must be exercised to prevent loss of ammonia and the end-point is rather unsatisfactory. In this work, the determinations were allowed to stand twenty-four hours, which gives practically identical results with the one-hour boiling modification used by Craig.² The boiling and cooling scheme suggested by the latter largely offsets the strongest advantage of the method, that of ease of manipulation. In the comparison of this method with that of Blank and Finkenbeiner's in the same article, the Legler method is shown to give slightly higher results. Though the two methods are in "practical accord" as he suggests, in the writer's comparisons the hydrogen peroxide method almost invariably gave higher results.

THE GRAVIMETRIC HEXAMETHYLENETETRAMINE METHOD.³

"Ten grams of the formaldehyde solution are weighed into a flask and treated with an excess of standard ammonium hydroxide solution. The corked flask is shaken at intervals for several days. By this means the whole of the formaldehyde is converted into hexamethylenetetramine. The solution is then transferred to a weighed platinum dish, evaporated at a low heat—below 100° C., nearly to dryness, and the drying finished in a desiccator."

¹ *Ber. d. chem. Ges.*, 16, 1333 (1883).

² *This Journal*, 23, 638 (1901).

³ *Annual Report, Conn. Expt. Station*, 1899, p. 143.

Haywood¹ has recently shown that this method is unsatisfactory, owing to the fact that there is a continual loss of weight of the hexamethylenetetramine when left in the desiccator. The following determination, made on Solution I, is typical of the results obtained by the author. After evaporating nearly to dryness, the dish was placed in a desiccator and weighed at intervals of forty-eight hours, the weights obtained giving the following percentages of formaldehyde:

Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
41.83	40.34	39.46	38.70	38.02	37.40	36.87
36.35	35.91	35.60	35.24	34.90

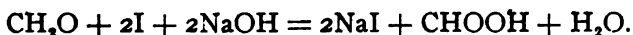
The weighing was here discontinued, as the last figures are obviously below the percentage of formaldehyde contained in the solution.

IODIMETRIC METHOD.²

The method used is a slight modification of the one originally proposed by Romijn,³ and is as follows:

"Thirty cc. normal sodium hydroxide and 5 cc. of the dilute formaldehyde solution are placed in a well-stoppered bottle and N/5 iodine (40 to 70 cc.) added until the liquid becomes yellow. After shaking for a minute, the liquid is acidified with 40 cc. of normal acid and the residual iodine titrated with N/10 thiosulphate. A blank titration should be made."

In the presence of an alkali, iodine acts indirectly as an oxidizing agent, giving, when formaldehyde is present, the iodide of the base and formic acid. The following equation illustrates the reaction:



A solution containing as much as 5 per cent. formaldehyde may be determined without dilution by this method, provided that not more than 2 grams of the solution are used. In the following table, weighed portions of the three strongest solutions were diluted to contain approximately 1 per cent. of formaldehyde and the diluted solutions were used for the analysis.

¹ Bulletin No. 73, Bureau of Chemistry, Department of Agriculture, "Report of Referee on Insecticides and Fungicides before Official Association of Agricultural Chemists," 1902.

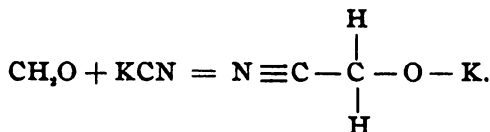
² *Ztschr. anal. Chem.*, 39, 60-63 (1900).

³ *Ibid.*, 36, 18-24 (1897).

I.	II.	III.	IV.	V.	VI.	VII.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
36.94	14.36	9.60	4.53	0.98	0.095	...
37.06	14.46	9.58	4.60	0.96	0.089	...
...	...	9.64	4.62	...	0.094	...

THE POTASSIUM CYANIDE METHOD.¹

This is another method which is applicable to solutions containing but small quantities of formaldehyde. According to the originator of the method it depends upon the fact that formaldehyde combines with potassium cyanide to form an additional product, represented by the following:



In the determination, the formaldehyde is mixed with a known quantity of potassium cyanide, the latter being in excess. If this mixture is added to an excess of silver nitrate the uncombined cyanide is precipitated as silver cyanide. By using a standard silver nitrate solution and titrating the excess, we can easily calculate the amount of potassium cyanide used by the formaldehyde, and accordingly can determine the amount of formaldehyde present. The method is as follows: Ten cc. of N/10 silver nitrate are treated with six drops of 50 per cent. nitric acid in a 50 cc. flask. Ten cc. of a solution of potassium cyanide (containing 3.1 grams of KCN in 500 cc. of water) are then added and well shaken. An aliquot portion of the filtrate, say 25 cc., is titrated according to the method of Volhard with an N/10 solution of ammonium sulphocyanate for excess of silver. Another 10 cc. portion of N/10 silver nitrate is acidified with nitric acid and treated with 10 cc. of the potassium cyanide solution to which has been added a measured quantity of the dilute formaldehyde solution. The whole is made to 50 cc. and a 25 cc. filtrate from it titrated with N/10 ammonium sulphocyanate for the excess of silver, as before. The difference between these two results multiplied by 2 gives the amount of potassium cyanide that has been used by the formaldehyde in terms of N/10 ammonium sulphocyanate.

¹ *Ztschr. anal. Chem.*, 36, 18-24 (1897).

In obtaining the following results, all solutions containing more than 1 per cent. were diluted.

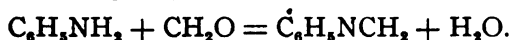
I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.	VII. Per cent.
37.12	14.40	9.61	4.60	1.002	0.102	0.0099
37.07	14.55	9.63	4.54	0.972	0.102	0.0099
37.18	14.48	9.59	4.64	0.99

With solutions of 1 per cent. strength it was found necessary to use 15 cc. of silver nitrate. It is preferable to add six or eight drops of nitric acid instead of two as used by Romijn, as the titration is sharper when the solution is more strongly acid. In working with Solution VII, a 200 cc. flask was used instead of the 50 cc. flask, and 100 cc. of the filtrate titrated.

Attention should be called to the fact that the directions for using this method, as given in Allen's "Commercial Organic Analysis,"¹ which were taken from a review that appeared in the *Analyst*,² are not explicit. The essential feature of the method being that formaldehyde forms an additional product with potassium cyanide, the formaldehyde solution must be mixed with the cyanide solution and the mixture added to the silver nitrate. This is not made clear in the article referred to. In the same translation another error is introduced in that the operator is told to dilute to 500 cc. instead of 50 cc., as in the original article.

THE ANILINE VOLUMETRIC METHOD.³

If formaldehyde be treated with an aqueous solution of aniline, methylene aniline is precipitated, as illustrated by the following:



Following is the method of procedure:

"Four hundred cc. of aniline solution, containing 3 grams of aniline per liter, are placed in a flask and 1 cc. of formaldehyde solution added, by drops, with shaking. The mixture is made up to 500 cc. and after some time filtered. The excess of aniline is then estimated in 50 cc., taking as the end-point that at which the red color acquires a strong bluish tone, remaining unaltered on further addition of acid."

The end-point in this titration is quite indefinite, the "bluish

¹ Third edition, p. 221.

² *Analyst*, 22, 221 (1897).

³ *Pharm. Ztg.*, 40, 611 (1895).

tone" developing very gradually. After repeated unsuccessful trials, the attempt to use the method was abandoned.

Four of the methods are summarized in the following table, which gives the average percentages of formaldehyde found in the solutions used, and also shows the working range of each when no dilutions are made.

Method.	I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.	VII. Per cent.
H ₂ O ₂	37.33	14.45	9.74	4.81
Legler	37.07	14.45	9.65	4.43
Iodimetric	4.55	0.97	0.093	...
Potassium cyanide	0.988	0.102	0.0099

The following conclusions may be drawn from the comparisons made:

First, the Blank and Finkenbeiner method is very satisfactory for strong solutions.

Second, the Legler method, while not giving quite as high results as the former, is fairly satisfactory.

Third, the gravimetric hexamethylenetetramine method is practically worthless.

Fourth, the iodimetric and the potassium cyanide methods give good results on dilute solutions. It should be remembered that in diluting strong solutions to the range of these methods, a small error in weighing may be considerably multiplied. The potassium cyanide method is best adapted to the estimation of very small quantities of formaldehyde, it being possible to determine with accuracy 1 part in 100,000.

Fifth, in the hands of the writer, the end-point of the aniline volumetric method was impossible to read.

Since preparing the foregoing paper there has come to my attention an article reviewed in the *Zeitschrift für angewandte Chemie*, April 7, 1903, the original article having appeared in the *Deutsche Gerber Zeitung*, 1-4, 6, 8, 12. The author, C. Wallnitz, has compared seven commonly used methods of determining formaldehyde and has arrived at the following conclusions: That the hydrogen peroxide and the iodine methods are superior to the others tested when the reagents are freshly prepared; that the ammonium chloride¹ method, the Legler ammonium method,

¹ Hugo Schiff: *Chem. Ztg.*, 27, 14, Jan. 7, 1903.

and the aniline volumetric method all lack distinctness in the end-point readings; and further, that the gravimetric silver nitrate method of L. Vanino is practically useless, not being exact in its results.

The potassium cyanide method, which is one of the most accurate, was not included in this investigation.

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THE ESTIMATION OF FORMALDEHYDE IN MILK.

BY BERNARD H. SMITH.

Received June 26, 1903.

FORMALDEHYDE is added to milk as a preservative more than to any other food. Its quantitative determination in this universally used product is, therefore, of the greatest importance.

Formaldehyde distils slowly even from an aqueous solution. When it is added to milk, and has combined to a greater or less extent with the albuminoids present, the rate of distillation is naturally slower still. Should the distillation be continued until four-fifths of the volume taken has been driven over, which is as much as can be distilled conveniently, all of the formaldehyde will not have been recovered. The distillation is, moreover, a troublesome one, owing to the frothing and bumping of the boiling milk. The writer has found that the latter can be largely obviated by using with the ordinary condenser a 500 cc. Kjeldahl nitrogen flask and a round, flat evaporating burner. With this apparatus the distillation proceeds quietly and without difficulty.

In an article by Leonard and Smith¹ results are given showing that the addition of "a few drops of dilute sulphuric acid" largely increased the amount of formaldehyde recovered during the first part of the distillation. In their experiments 100 cc. of milk were used containing 1 part in 100,000 of formaldehyde, and three portions of the distillate of 20 cc. each were collected. Nearly one-third of the formaldehyde present was found in the first 20 cc. of the distillate.

In attempting to make use of this suggestion the writer found that the amount of sulphuric acid present had a great influence on the amount of formaldehyde found in the first 20 cc. of the distillate, as is shown by the following table:

0.3 cc. dilute H_2SO_4 (1 : 3). Per cent.	1 cc. dilute H_2SO_4 (1 : 3). Per cent.	5 cc. dilute H_2SO_4 (1 : 3). Per cent.	20 cc. H_2SO_4 not diluted. Per cent.
24	32.5	18	None

This would tend to show that in obtaining maximum results the quantity of sulphuric acid added is an important factor, and that while the milk should be more than simply acid, an excess of

¹ *Analyst*, 22, 5 (1897).

acid is to be avoided. In subsequent work, 1 cc. of sulphuric acid of a dilution of 1 : 3 was used with 100 cc. of milk. One-fifth portions, or 20.02 cc. were collected and analyzed, using the potassium cyanide method.¹

The following work was undertaken in an attempt to decide as to whether milk, containing formaldehyde, would yield the same amounts in the first 20 cc. of distillate, after standing some time, as upon immediate distillation, and also as to whether different samples of milk containing various amounts of formaldehyde would give it up in the first 20 cc. of the distillate in direct proportion to the amount they originally contained.

Four samples of fresh milk were treated with formaldehyde so that they contained 1 part in 5,000, 1 part in 10,000, 1 part in 25,000, and 1 part in 50,000. One hundred cc. portions of each were distilled immediately, others at the end of twenty-four and forty-eight hours. The latter in the intervening time were kept in a cool place. The following percentages of the total formaldehyde added were obtained in the first 20 cc. of the distillates.

	1 part in 5,000. Per cent.	1 part in 10,000. Per cent.	1 part in 25,000. Per cent.	1 part in 50,000. Per cent.	Averages. Per cent.
Determined immediately..	31.50	33.90	36.10	41.00	35.62
After 24 hours	30.60	32.00	32.80	37.50	33.22
After 48 hours	30.75	31.50	35.00	36.00	33.31

From the average column on the right, it is seen that the average results on milk that has stood a short time after the addition of the formaldehyde are very close to 33 $\frac{1}{2}$ per cent. The next column shows that the samples of milk containing the least formaldehyde give the highest percentages of the total amount present. The table shows, furthermore, that if milk containing formaldehyde is kept cool, it may stand one or two days at least without altering the amount obtained on analysis. A trial proved that when milk containing formaldehyde is subjected to a warm and varying temperature, the amount of formaldehyde recovered by distillation in the first 20 cc. decreases so that at the end of forty-eight hours only 18 or 20 per cent. will be found, instead of approximately 33.

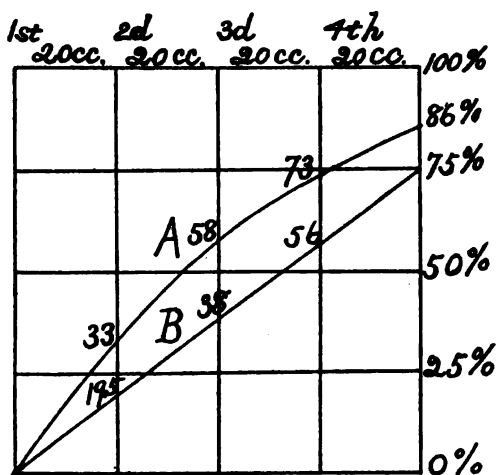
The following chart, the data for which were compiled from a number of analyses, gives the curves showing the rapidity of the

¹ See the preceding paper, p. 1032.

distillation of formaldehyde from milk containing 1 part in 10,000. The ordinates represent the per cent. of the total formaldehyde present, and the abscissas the amount of distillates.

The line A is the curve obtained from milk after the addition of 1 cc. of the dilute acid, while B is the one obtained from milk without the addition of acid.

In summarizing, it may be said that considerable time and trouble may be saved by using a Kjeldahl flask and a round, flat



evaporating burner in the distillation of milk; that the quantity of sulphuric acid added has a decided effect upon the amount of formaldehyde obtained in the first part of the distillation; that if the treated milk is kept in a cool place, the percentage of formaldehyde found will remain practically constant for at least forty-eight hours; and that where 100 cc. of milk are treated with 1 cc. of sulphuric acid of a dilution of 1 : 3 and distilled, the first 20 cc. of the distillate will contain very close to 33 $\frac{1}{2}$ per cent. of the total formaldehyde present.

The author wishes to acknowledge the valuable suggestions of Dr. H. W. Wiley, under whose direction this and the foregoing article have been prepared.

THE ELECTROLYTIC PRECIPITATION OF NICKEL FROM PHOSPHATE SOLUTIONS.¹

BY WALTER T. TAGGART.

Received July 6, 1903.

NICKEL has been quantitatively precipitated in the electrolytic way from various electrolytes.¹ The purpose of this particular investigation was to ascertain the exact conditions under which this metal could be deposited from phosphate solutions without carrying down phosphorus with it; also to effect, if possible, separations of nickel from other metals in the same electrolyte. The method pursued consisted in precipitating nickel sulphate solutions with varying amounts of disodium hydrogen phosphate of 1.038 specific gravity, dissolving the precipitate in phosphoric acid of 1.347 specific gravity, and after dilution with water, electrolyzing the solutions with varying current and pressure conditions.

The precipitations were made in platinum dishes—the cathodes, while flat platinum spirals were used as anodes. The deposits were treated as ordinarily directed in electrolytic work. The details of more than forty experiments appear in those recorded in the accompanying tables, with sufficient minuteness to enable any person, so desiring, to repeat them with the confidence of obtaining like satisfactory results.

EXPERIMENTS.

	1.	2.	3.	4.	5.	6.
N.D. ₁₀₀	2.0	2.0	4.0	4.0	2.0	3.0
Volts	6	6	6	6	6	6
Dilution, cc.	225	125	200	250	125	175
Temperature	50°	65°	65°	55°	65°	65°
Time, hours	7	7½	8¼	9½	6¾	8½
Na ₂ HPO ₄ , cc.	90	90	130	180	90	135
H ₃ PO ₄ , cc.	4.5	4.5	9.0	9.0	4.5	6.75
Nickel taken, gram .	0.2166	0.2166	0.4332	0.4332	0.2166	0.3249
Nickel found, gram .	0.2163	0.2161	0.4298	0.4321	0.2165	0.3253

¹ From the author's thesis for the Ph.D. degree.

² See Smith's "Electrochemical Analysis," p. 91, third edition, 1902.

	7.	8.	9.	10.	11.
N.D. ₁₀₀	4.0	2.0	3.0	3.0	4.0
Volts	6	6	6	6	6
Dilution, cc	250	125	175	175	250
Temperature	55°	65°	70°	62°	55°
Time, hours	9½	7¼	9	9½	9¼
Na ₂ HPO ₄ , cc	180	90	135	135	180
H ₃ PO ₄ , cc	9.0	4.5	6.75	6.75	9.0
Nickel taken, gram	0.4332	0.2166	0.3249	0.3249	0.4332
Nickel found, gram	0.4327	0.2163	0.3247	0.3251	0.4321

	12.	13.	14.	15.	16.
N.D. ₁₀₀	1.-1.75	1.4-1.8	1.0-1.5	1.4-1.8	1.25
Volts	6	6	6	6	6
Dilution, cc	125	125	175	175	175
Na ₂ HPO ₄ , cc	90	90	90	135	90
H ₃ PO ₄ , cc	4.5	4.5	4.5	6.75	4.5
Nickel taken, gram .	0.2176	0.2176	0.2176	0.3264	0.2176
Nickel found, gram .	0.2179	0.2181	0.2176	0.3271	0.2180
Temperature	56°	50°	50°	50°	50°
Time, hours	7	7	7	9¼	7¼

	17.	18.	19.	20.	21.
N.D. ₁₀₀	1.4-1.8	1.25-1.6	1.25-1.6	0.25-1.6	1.25-1.6
Volts	6	6	6	6	6
Dilution, cc	225	230	230	230	230
Na ₂ HPO ₄ , cc	135	180	180	180	180
H ₃ PO ₄ , cc	6.75	9.0	9.0	9.0	9.0
Nickel taken, gram .	0.3264	0.4352	0.4352	0.4352	0.4352
Nickel found, gram	0.3271	0.4353	0.4355	0.4353	0.4354
Temperature	50°	50°	50°	50°	50°
Time, hours	9	10	10	10	10

In every case except No. 1 and No. 11 the precipitation was complete. The success of the process depends greatly on keeping the dish covered and washing down its sides with water at frequent intervals, to supply the loss by evaporation and to prevent the phosphate of nickel from separating out on the dish.

These results need no further explanation. The deposits were equal in appearance, if not superior, to any deposits of nickel ever obtained in this laboratory. Those of 0.4352 gram of nickel, when dissolved in nitric acid and tested with ammonium molybdate, showed but a trace of phosphorus, which is without influence, for solutions electrolyzed by Fresenius and Bergmann's method¹ gave exactly the same amount of nickel.

The influence of elevation of temperature is shown in the following examples:

¹ *Ztschr. anal. Chem.*, 19, 320.

	22.	23.	24.
N.D. ₁₀₀	2.4-2.8	2.25	1.80-2.75
Volts	6	6	6
Dilution, cc.	125	175	225
Temperature	88°	88°	88°
Time, hours	2½	5	6¼
Na ₂ HPO ₄ , cc.	90	135	180
H ₃ PO ₄ , cc.	4.5	6.75	9
Nickel taken, gram.....	0.2176	0.3264	0.4352
Nickel found, gram.....	0.2167	0.3265	0.4331
	25.	26.	27.
N.D. ₁₀₀	1.80-2.75	1.80-2.75	1.80-2.75
Volts	6	6	6
Dilution	125	125	175
Temperature	82°	80°	80°
Time, hours.....	3½	4	5½
Na ₂ HPO ₄ , cc.	90	90	135
H ₃ PO ₄ , cc.	6.75	5.6	9.1
Nickel taken, gram.....	0.2176	0.2176	0.3264
Nickel found, gram.....	0.2150	0.2161	0.3255

The precipitation was only complete in 23. If the conditions there given be adopted, satisfactory results can be obtained in a considerably shorter time than is required when working at the ordinary temperature.

The separation of nickel from manganese, iron, aluminum and chromium was considered. The results were negative in each instance.

Hence, it may be concluded from what has preceded that nickel free from phosphorus can be completely precipitated from a solution of nickel sulphate containing disodium hydrogen phosphate and free phosphoric acid, a mineral acid; that the deposit is equal to that precipitated by any other known method; that the time factor can be reduced by raising the temperature and that nickel can not be separated from manganese, iron, aluminum or chromium in phosphoric acid solutions. It was found that chromium salts in the presence of disodium hydrogen phosphate and free phosphoric acid are oxidized to chromates by the electric current.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 74.]

THE REDUCTION OF NITRIC ACID IN METALLIC NITRATES TO AMMONIA BY THE ELECTRIC CURRENT.¹

BY WM. H. EASTON.

Received July 4, 1903.

LUCKOW announced² that "dilute nitric acid between two platinum poles will not be reduced to ammonia either alone or in the presence of dilute sulphuric acid. But, if copper sulphate in solution be added to the dilute nitric acid, then the formation of ammonium sulphate occurs, when the liquid is electrolyzed." Vortmann³ endeavored to make this a quantitative method for the estimation of nitric acid.⁴

This is his description of the analysis of a nitrate:

"The solution of the nitrate is placed in a platinum vessel with a sufficient amount of pure copper sulphate and it is then electrolyzed. It is advantageous to use a feeble current (1 to 2 cc. of oxyhydrogen gas per minute). When all of the copper is deposited, the residual liquid is evaporated to a small bulk and the ammonia distilled off as usual."

Simple as these directions are, many persons have failed to get satisfactory results. Numerous inquiries have been made at this laboratory for fuller details; hence, the writer was directed to give the problem attention, more particularly with reference to the factors which have never before been studied in this particular example, *viz.*, *amperage, time, current density at the anode, the amount of copper sulphate essential, the amount of nitrate and the character of the cathode.*

Potassium nitrate was the first nitrate analyzed. The conditions were:

Potassium nitrate.....	0.5 gram
Copper sulphate	0.5 gram
Cathode.....	Platinum or copper plate of 100 square centimeters area.
Amperes	0.15 to 3.0
Time	for 3.0 amperes, 1¼ hours for 0.15 ampere, 8½ hours

¹ From the author's thesis for the Ph.D. degree.

² *Ztschr. anal. Chem.*, 19, 11 (1880).

³ *Ber. d. chem. Ges.*, 1890, p. 2798.

⁴ See Smith's "Electrochemical Analysis," p. 194, third edition, 1902.

Volts: From 3 to 8, depending upon the current strength.

Dilution: 150 cc.

Sulphuric acid (sp. gr. 1.062): 30 cc.

The following percentages of nitrogen reduced to ammonia were obtained, the theoretical per cent. in potassium nitrate being 13.86:

13.70	13.60	13.50	13.65
13.74	13.68	13.77	13.54
13.62	13.43	13.32	13.68
13.43	13.78	13.50	

It was further learned, from additional experiments, that the time factor could be reduced to two and one-half hours by employing a current of 1 ampere. Further, in no trial did the variation of the current density at the anode have any influence on the amount of nitrogen reduced to ammonia. The amount of copper sulphate needed can easily be deduced from the results which follow, the other conditions being as recorded above.

Grams KNO_3 .	Grams $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.	Per cent. N reduced.
0.5195	0.1098	11.44
0.5243	0.2083	12.23
0.5041	0.2600	13.33
0.4950	0.3600	13.13
0.5676	0.5691	13.74

Theory, 13.86 per cent.

The quantity of potassium nitrate was also varied, equal weights of copper sulphate being taken, while the other conditions continued as before:

Grams of potassium nitrate.	Grams of nitrogen reduced.	Per cent. of nitrogen reduced.
0.1053	0.0148	14.01
0.1063	0.0148	13.93
0.2592	0.0348	13.43
0.2616	0.0356	13.62
0.5027	0.0693	13.77
0.5723	0.0789	13.78

The method seems accurate enough for all quantities. The actual weights of nitrogen show the delicacy of the method.

In the preceding experiments platinum dishes were the cathodes. The copper deposits were compact and readily washed. When copper plates of 100 sq. cm. area were substituted for the dishes and suspended in the nitrate solution, contained in beakers, the

precipitated copper was spongy, did not adhere well, and some difficulty was had in washing it. The percentages of reduced nitrogen ranged from 13.04 to 13.44 (theory, 13.86). Lead plates of 100 sq. cm. area were also tried. The copper was precipitated upon them in a very unsatisfactory form. They were also attacked, and the nitrate was never completely reduced when they were employed. No better success was met with mercury cathodes, while nickel (36 sq. cm. area) proved very satisfactory.

The time necessary for the reduction of 0.5 gram of potassium nitrate was two and one-half hours, when using a current of 1 ampere. Would 3 or 5 amperes produce the desired result in a shorter period? Accordingly, a solution of 0.5009 gram of potassium nitrate, 1 gram of copper sulphate and 40 cc. of sulphuric acid (sp. gr. 1.062) was electrolyzed for thirty minutes with a current of 3 amperes. The copper was not completely precipitated and only 6.68 per cent. of the nitrogen was reduced to ammonia. Upon increasing the current to 5 amperes and allowing it to act for thirty minutes the percentage of reduced nitrogen was 13.22, although not quite all of the copper was precipitated.

It was a matter of considerable interest to learn the behavior of other nitrates than those of the alkali metals. Copper nitrate electrolyzed alone—without copper sulphate—yielded 11.52 and 11.35 per cent. of nitrogen (theory, 11.59 per cent.) to the current. In the case of silver nitrate, complete reduction was not reached until after the addition of an equal amount of copper sulphate. This proved to be the case with cobalt and cadmium nitrates.

Observing the conditions given on p. 1042, employing at the same time a current of $N.D_{100} = 1$ ampere, the reduction will proceed rapidly and the method will prove very helpful in many instances.

Experiments have been made with a rotating anode which suggest the possibility of reducing quite considerably the time factor in this method.

THE ELECTROLYTIC DETERMINATION OF MANGANESE AND ITS SEPARATION FROM IRON AND ZINC.¹

BY GEORGE P. SCHOLL.

Received July 6, 1903.

THE deposition of manganese as peroxide for quantitative estimations by electrolysis has been the subject of a great deal of investigation, as reference to its voluminous literature will disclose.¹

It was believed that formic acid, because of its simple constitution, would prove an excellent electrolyte and that under the right conditions very satisfactory results would be obtained with it. It was, therefore, tried with the addition of sodium formate.

The electrolysis was conducted as follows: Ten cc. of a solution of manganese sulphate (= 0.1100 gram of metal) were mixed with 5 cc. of formic acid (sp. gr. 1.06), 10 cc. of a sodium formate solution, containing 1 gram of the salt, and diluted to 130 cc. with water so that the liquid covered 100 sq. cm. of the surface of the dish. The dish was made the anode and a flat spiral the cathode, arranged as nearly as possible equidistant from the sides and the bottom of the dish to obtain as uniform a distribution of the current as possible. The current equaled 1.4 amperes, the pressure between the electrodes being 12 volts at the beginning but decreasing to 8.6 volts at the end. It acted for one and one-half hours, when, no further precipitation taking place, the liquid was siphoned off and replaced by water without interrupting the current. The deposit showed a deep black, shining color. It adhered firmly to the dish and was not detached on washing. Smith's statement¹ that it is useless to try to obtain a definite compound by drying the deposit and that ignition to the protosesquioxide is necessary to secure definite and concordant results was found to be true. The results of four determinations made in exactly the same manner were:

Electrolyte.	Time.	Temperature.	N.D. ₁₀₀ at anode.	Voltage.	Mn found. Gram.
10 cc. MnSO ₄ + 5 cc. HCOOH 1.06 sp. gr. + 10 cc. = 1 gm. sodium formate.	1 1/2 hrs.	Ordinary temp. at start, heated up by action of current to 40°- 50° at the end.	1.4	12 volts at start to 8.6 volts at end.	0.1100 0.1105 0.1104 0.1101

¹ From author's Ph.D. thesis.

² Consult Smith's "Electrochemical Analysis," Third edition, 1902.

³ "Electrochemical Analysis," Third edition, p. 96.

These demonstrated that it was quite possible to deposit the manganese completely in the presence of formic acid, even if the latter was present in amounts considerably above those given by Kaepfel as the maximum.¹

According to Classen² it is necessary to weigh the platinum dish after the deposit of peroxide has been removed from it, as the dish suffers a diminution of weight during electrolysis, amounting to about 1 mg. With the electrolyte used in the preceding experiments this did not take place, the dish losing either no weight at all or at the most only 0.1 mg.

The deposits were weighed without any difficulty. They slowly attracted moisture, however, and on standing over night gained perceptibly in weight.

Experiments were also conducted with low voltage to ascertain the effect of a lower current and consequently lower current density upon the deposit. The character of the latter remained unchanged. The application of heat (50° to 55°) proved harmful. It was also ascertained that large quantities of sodium formate retarded the precipitation quite decidedly. Further, the weights of the deposits increased as the amount of sodium formate was increased. Indeed, it was scarcely possible to weigh those obtained where 2.5 grams of sodium formate had been present, even after ignition over a blast-lamp. The most reasonable explanation of this fact seemed to be that the sodium formate was partly decomposed by the current, with the formation of caustic soda at the cathode. This caustic soda, being specifically heavier than the electrolyte, fell to the bottom of the dish anode, and was enclosed and held mechanically by the precipitating manganese peroxide. It should be noted in this connection that careless washing of the deposit was entirely excluded.

The next step was, consequently, to do away with the source of error-traceable to the addition of sodium formate and to try formic acid alone. The voltage required was high, on account of the low conductivity of the formic acid, it being 17.5 volts between the electrodes at the start, with a current strength of 1 ampere. As the solution became very warm in about an hour, the voltage was decreased to 7.9 volts, giving an amperage of 0.8. The deposit did not come down as quickly as when sodium formate was pres-

¹ *Ztschr. anorg. Chem.*, 16, 268.

² "Ausgewählte Methoden," p. 369.

ent, but the manganese was all out after four hours. It was further found that the precipitate was absolutely non-hygroscopic after ignition, and could be weighed with perfect ease. It was left purposely exposed to the action of the atmosphere over night and reweighed on the following morning, when the weight was found to be the same. The appearance of the deposit was like that noticed before. As the determinations with employment of the spiral of platinum wire as cathode had necessitated such a high potential between the electrodes in order to obtain the necessary strength of current and caused thereby objectionable heating of the electrolyte, it was decided to adopt some means to get along with as low a voltage as possible, and which would give the necessary current. Accordingly, a so-called basket electrode was used. This was a platinum dish, which conformed in shape to the interior surface of the roughened dish on which the precipitation of manganese peroxide took place. It had an area of 60 sq. cm. and was perforated with holes to allow of a better egress of the gases set free during electrolysis and a better mixing of the solution. The following table gives the results of some experiments carried out with varying quantities of formic acid and varying quantities of manganese.

The deposits obtained were all very satisfactory and adherent. A slight disposition towards loosening was noticeable with those in which there was 0.2880 gram of manganese protosesquioxide present. It was, however, very slight, and, owing to the scaly nature of the material, it was quite easy to filter it out quickly on a small filter, wash, dry and remove it from the filter and add it to the bulk of the material in the dish, together with the ash of the filter-paper.

It is also apparent from the above table that the addition of more than 5 cc. of formic acid of 1.06 specific gravity has no beneficial effect. On the contrary, larger amounts of formic acid tend to retard the precipitation. Much less than 5 cc. of formic acid cannot be used, as there is a tendency to form flakes of a brown precipitate around the cathode, which have to be brought into solution again by the addition of more formic acid.

Other experiments were made to learn whether the addition of ammonium formate would have any accelerating or otherwise beneficial effect on the deposit. Such was not found to be the case. When chrome alum was introduced into the electrolyte, the

Manganese taken. Gram.	Manganese found. Gram.	Formic acid (sp. gr. 1.09).	Time.	Temp. ordinary, rising toward the end.	N.D.no.	Voltage.	Character of deposit.
0.1034	0.1036	5	2½		0.8 to 1.0	7.6 at end.	satisfactory, adherent
0.1034	0.1034	5	2½	"	0.8 to 1.0	7.6	"
0.1034	0.1034	5	2½	"	0.8 to 1.0	7.6	"
0.1034	0.1035	5	2½	"	0.8 to 1.0	7.6	"
0.1034	0.1033	5	2½	"	0.8 to 1.0	7.6	"
0.1034	0.1035	10	3½	"	0.8 to 1.0	7.2	"
0.1034	0.1034	10	3½	"	0.8 to 1.0	7.2	"
0.1034	0.1032	15	5	"	0.8 to 1.0	7.0	"
0.1551	0.1551	5	3¼	"	0.8 to 1.0	7.3	"
0.1551	0.1552	5	3¼	"	0.8 to 1.0	7.3	"
0.1551	0.1550	7½	4	"	0.8 to 1.0	7.0	"
0.1551	0.1449	10	5	"	0.8 to 1.0	6.8	"
0.2068	0.2069	5	5	"	0.8 to 1.0	6.6	" a trifle loose on washing.
0.2068	0.2069	5	5	"	0.8 to 1.0	6.6	"
0.2068	0.2070	10	6¼	"	0.8 to 1.0	5.6	"
0.2068	0.2071	10	6¼	"	0.8 to 1.0	5.6	"
0.2068	0.2071	15	7	"	0.8 to 1.0	5.4	"

results were also very unsatisfactory. It may, therefore, be briefly concluded that:

(1) The statement of Kaepfel, that it is not possible to precipitate manganese completely in the presence of formic acid and that more than five drops of this acid prevent the deposition of manganese peroxide entirely, is not borne out by the experimental facts.

(2) It is possible to obtain the deposit of peroxide from a formic acid solution in a beautifully adherent and satisfactory form, which can be washed and ignited without any trouble.

(3) Formic acid is a better electrolyte than acetic acid, it being possible, according to Classen,¹ to deposit not more than 0.08 gram of manganese in the form of peroxide when the latter is used.

The influence of other organic acids upon the precipitation of manganese was also studied. These were propionic, butyric, malonic, succinic, tartaric and fumaric acids. Fumaric acid, alone, yielded results which were in the least satisfactory. The deposits were never entirely adherent.

(1) SEPARATION OF MANGANESE AND IRON.

It seemed very probable that iron might be easily separated from manganese in a formic acid solution. This hope, however, seemed doomed to disappointment, for when a separation was tried under the conditions which had proved most successful for manganese alone, not much of a result was obtained, even upon continuing the electrolysis for twelve hours. The electrolyte consisted of 10 cc. of a ferric ammonium sulphate solution, containing 0.1000 gram of metallic iron, 10 cc. manganese sulphate, containing 0.1034 gram manganese and 5 cc. formic acid. The basket electrode served as cathode and the dish as anode. A long series of experiments was made, but the results were far from quantitative. It was also tried to see whether a uniform current density at the electrodes would prove beneficial, and therefore a number of experiments were made by introducing the solution into a beaker glass and suspending in it two platinum gauze electrodes, arranged exactly opposite each other. This was unsuccessful. It was noticed in all of this work that, in order to obtain the iron free from manganese, it was absolutely essential to have the current density at the cathode entirely uniform, that is to say, all parts of the cathode had to be equidistant from the anode surface.

¹ "Quantitative Analysis by Electrolysis," p. 149.

If there was one point of the cathode nearer to the anode, there was danger of some manganese peroxide being deposited there. Perhaps this fact explains why it has not been possible to obtain concordant results with methods proposed by different investigators up to the present time.

Electrodes of sheet platinum were also tried. The results were disappointing. It was next decided to ascertain whether the separation of the two metals could be made by retarding or preventing the deposition of manganese dioxide altogether. Hence the electrolysis was conducted thus: The electrolyte contained 10 cc. of manganese sulphate (= 0.1034 gram of manganese) and 10 cc. of a ferric ammonium sulphate solution containing 0.1003 gram of iron. To this were added 10 cc. of an ammonium formate solution, and 10 cc. of an ammonium sulphate solution containing 3 grams of this salt. 1 cc. of a solution of 45 per cent. formaldehyde was also added. The platinum dish was used as cathode, and the basket electrode, which had been used before, was introduced as anode. The solution was then made up to 130 cc., and the electrolysis conducted in the cold, with a voltage between the electrodes of 3.5 and an amperage of 1.4, the $N.D_{100}$ at the anode being consequently 2.33 and at the cathode 1.4. The iron was deposited in from three to five hours in a very satisfactory form, and not a trace of it could be detected in the solution. It proved to be entirely free from manganese. A little manganese peroxide precipitated on the anode in a very adherent form, but only from 0.0055 to 0.006 gram of peroxide had deposited at the end of the electrolysis when the iron was fully precipitated. No peroxide was suspended in the electrolyte. The solution was colored red from the permanganic acid formed. The deposit of iron contained varying and sometimes considerable amounts of carbon, which proved, however, no obstacle to a successful determination of this metal, as it was easily possible to dissolve the deposit off the dish very quickly by introducing distilled water and a few cubic centimeters of concentrated sulphuric acid. The solution was then transferred to a beaker and boiled for a few minutes in order to get rid of the hydrocarbons. A little granulated zinc was added in order to reduce any iron which might have become oxidized, and the solution was then titrated with a very dilute standardized solution of potassium permanganate. The whole manipulation in this way consumed, perhaps, less time than the

Iron present. Gram.	Iron found. Gram.	Manganese present. Gram.	Tartaric acid. Gram.	Ammonium formate. cc.	Formaldehyde 45 per cent. cc.	Ammonium sulphate. Grams.	Time.	Temp.	N.D. ₁₀₀	Voltage.
0.1003	0.1001	0.1034	1	10	1	3	4	ordinary	1.4	3.5
0.1003	0.1003	0.1034	1	10	1	3	4 1/4	"	1.4	3.5
0.1003	0.0999	0.1034	1	10	1	3	3 1/2	"	1.4	3.5
0.1003	0.0999	0.1034	1	10	1	3	4	"	1.4	3.5
0.1003	0.1001	0.1034	1	10	1	3	4	"	1.4	3.5
0.1003	0.1001	0.1034	1	10	1	3	4	"	1.4	3.5
0.0982	0.0982	0.1034	1	10	1	3	4	"	1.4	3.5
0.0982	0.0983	0.1034	1	10	none	3	4	"	1.4	3.5
0.0982	0.0982	0.1034	1	10	none	3	4	"	1.4	3.5
0.0982	0.0978	0.1034	1	10	1	3	4	"	1.4	3.5
0.0982	0.0980	0.1034	1	10	1	3	4	"	1.4	3.5

drying and weighing of the dish would have done. The following results were obtained in this manner:

The solution, when removed, had a fishy smell, due to decomposition products of the formaldehyde. The addition of the latter was discontinued after it had been shown by experiment that its presence had no influence on the result. The fishy smell of the solution did not appear after its removal. Results with and without formaldehyde are given in the above table.

Though it was shown by these experiments that, in an electrolyte composed as above, a successful separation of the iron and manganese could be accomplished in much less time than by the method of Kaepfel, yet it was felt that only half of the problem had been solved in this way. The fact that the manganese could not be determined electrolytically after the iron was all out, and that it had to be held up and thus be prevented from deposition, were sufficient stimulants to renew the effort of finding a method by which the two metals could be determined simultaneously.

The experiments with formic acid were, therefore, resumed. The electrolysis was carried out in the roughened platinum dish with the basket platinum electrode, it having been found by repeated trials that a spiral cathode could not be used, as there was invariably a precipitate of manganese oxide on it, especially on the outer rim, which was nearest to the anode, due evidently to a high current density at the cathode. The electrolyte was made up in such a manner that 10 cc. of a solution, containing 0.1 gram of sodium sulphite, were introduced into the dish and the ferric ammonium sulphate, containing 0.0997 gram of iron, was added. The solution immediately acquired a very dark red color. The 10 cc. of manganese sulphate were then introduced, and after that the formic acid solution. Five cc. of the latter acid of 1.06 sp. gr. were found to answer well. It was discovered that the addition (twice) of 1 cc. of a sodium sulphite solution, containing 0.1 gram in 1 cc. for every half hour at the beginning, and an addition of an equal amount every hour until the iron was out, was very beneficial. A very good indication of the gradual deposition of the iron is furnished by the fact that on each addition of sodium sulphite the color of the solution deepens quite perceptibly, the color getting paler, the less iron there is present. It should then be watched and tested for iron from time to time,

until no further reaction is obtained. Care must be taken in this connection that the electrode with the iron deposit on it be taken out as soon as the reaction of iron ceases. If that is not done, there is danger of some of the iron going into solution again. The basket electrode is then removed, washed off, and an auxiliary spiral electrode inserted as quickly as possible into the solution in order to prevent the manganese peroxide from dissolving in the electrolyte. Care must be taken during the time that this spiral electrode is in the solution, to insert resistance into the circuit, so as to cut down the current to 0.1 ampere or less, in order to prevent any precipitation on the spiral electrode. If this precaution be not taken, there will invariably be a brown-looking deposit on the electrode. The basket electrode with the deposit of iron on it is introduced into a small beaker and covered with distilled water. A few cubic centimeters of concentrated sulphuric acid are then added, when the solution of the iron will take place rapidly. The basket is then washed off and reintroduced into the electrolyte, after the spiral electrode has been taken out. Five cc. of formic acid of 1.06 sp. gr. are added, and the current raised to its original value again for the purpose of precipitating the rest of the manganese. The results obtained are shown in the following table and are very satisfactory and concordant.

Fe present. Gram.	Fe found. Gram.	Mn present. Gram.	Formic acid 1.06. cc.	Sodium sulphite.	Time.	Temp.	N.D.P. cathode.	Volt- age.
0.1010	0.1008	0.0988	5	6 additions 0.1 g. each	4½	ordinary	1.2	4.4
0.1010	0.1008	0.0988	5	0.1 "	5	"	1.2	4.4
0.1010	0.1010	0.0988	5	0.1 "	5	"	1.2	4.4
0.1010	0.1008	0.0988	5	0.1 "	5	"	1.2	4.4
0.1010	0.1011	0.0494	5	0.1 "	4½	"	1.2	4.4
0.1010	0.1007	0.0494	5	0.1 "	4½	"	1.2	4.4
0.1010	0.1010	0.0494	5	0.1 "	5	"	1.2	4.4
0.1010	0.1009	0.0988	5	0.1 "	5	"	1.2	4.4
0.1010	0.1011	0.0988	5	0.1 "	5	"	1.2	4.4
0.1010	0.1007	0.0988	5	0.1 "	5	"	1.2	4.4
0.1010	0.1011	0.0988	5	0.1 "	5	"	1.2	4.4

It was thus established that the separation of iron and manganese could also be effected in an electrolyte, consisting mainly of formic acid. It was noticed, however, that while the sodium sulphite was very effective, so far as the iron was concerned, it retarded the deposition of the manganese. The complete pre-

precipitation of 0.0988 gram of manganese required from thirteen to fourteen hours, a period almost too long to make the method of practical value. Therefore, further experiments were undertaken to reduce the time actually required for the precipitation of the manganese after the previous removal of the iron. Various means were adopted to accomplish this.

An experiment was conducted in the usual manner with addition of sodium sulphite, until the iron was out and removed. Ten cc. of an ammonium acetate solution were then added and the electrolysis continued. The result was quite surprising, for after two hours the level of the solution was raised, and it was observed that there was no further precipitation of manganese peroxide. When the solution was tested, no manganese was found to be present. The time of deposition of the peroxide had thus been reduced from thirteen or fourteen hours to seven hours. The deposit weighed 0.0992 gram while 0.0988 gram was present.

It was recognized that the presence of sodium sulphite in the electrolyte was not desirable and that it would be better, in order to remove all possible sources of error, if the separation could be effected without its use. Accordingly, ammonium acetate was introduced from the start and the quantity of sodium sulphite was cut down to 0.3 gram and then to 0.2 gram. For precaution's sake the basket electrode, with the major part of the iron on it, was also removed, but it was found that 93 per cent. of the iron had been deposited in two hours, and the rest was found when the electrode was removed at the end of the electrolysis. The surprising result was that the iron and manganese were all out of the solution at the end of four hours. These facts led to arranging the final experiments as follows: Ten cc. of manganese sulphate solution, 10 cc. of a ferric ammonium sulphate solution, 5 cc. of formic acid (sp. gr. 1.06) and 10 cc. of an ammonium acetate solution, after dilution were electrolyzed with a current of 1.1 amperes, with a pressure of 3.9 volts between the electrodes, for five hours. At the end of this time the level of the solution was raised, when no further precipitation took place. The solution was then siphoned off as before, both of the electrodes washed carefully and the iron titrated in the usual manner, while the manganese peroxide was ignited and weighed. The following table shows the close agreement of the results obtained:

Fe present. Gram.	Fe found. Gram.	Mn present. Gram.	Mn found. Gram.	Ammonium acetate.	Formic acid 1.06 sp. gr. cc.	Time. Hours.	Temperature.	N.D. ₁₀₀ at anode.	N.D. ₁₀₀ at cathode.	Voltage between electrodes.
0.0996	0.0996	0.0988	0.0990	10 cc. + 10 drops Na_2SO_4 .	5	4	ordi- nary.	1.1	1.83	3.9
0.0996	0.0994	0.0988	0.0991	"	5	4	"	1.1	1.83	3.9
0.0996	0.0994	0.0988	0.0986	10 cc., no Na_2SO_4 .	5	5	"	1.1	1.83	3.9
0.0996	0.0995	0.0988	0.0988	"	5	5	"	1.1	1.83	3.9
0.0996	0.0995	0.0988	0.0990	"	5	5	"	1.1	1.83	3.9
0.0996	0.0994	0.0988	0.0990	"	5	5	"	1.1	1.83	3.9

The deposit of iron had a shining, metallic appearance while the manganese peroxide was black, lustrous, and adherent to the dish.

(2) SEPARATION OF MANGANESE AND ZINC.

A solution of zinc sulphate, containing 0.1 gram of metal in 10 cc., was used. The electrolysis was carried out in a roughened platinum dish serving as anode, while the platinum basket electrode was connected as cathode. It was found that the deposit of zinc showed an extreme tendency to come down in spots upon the cathode, and the basket electrode had to be carefully adjusted so that it was equidistant from the sides of the dish. In this case the addition of ammonium formate exerted beneficial influence on the character of the zinc deposit, the best results being obtained with a solution containing 0.1034 gram of manganese, 0.1000 gram of zinc, 10 cc. of formic acid (sp. gr. 1.06), and 5 cc. of a solution of ammonium formate obtained by neutralizing formic acid (sp. gr. 1.06) with ammonia.

Mn present. Gram.	Mn found. Gram.	Zn present. Gram.	Zn found. Gram.	Time. Hours.	Temperature.	N.D. ₁₀₀ anode.	N.D. ₁₀₀ cathode.	Voltage.
0.1034	0.1037	0.1000	0.0998	11	ordinary	1.0	1.66	5.4
0.1034	0.1033	0.1000	0.1001	11½	"	1.0	1.66	5.4
0.1034	0.1036	0.1000	0.1003	11	"	1.0	1.66	5.4

The writer feels justified in claiming that the present investigation has conclusively proved that not only can manganese be easily and accurately determined in the electrolytic way in a formate solution, but that it can also be completely separated in a very simple manner from iron. Indeed, when compared with

any other gravimetric procedure which has been employed for the separation of these metals the electrolytic method is superior in every particular. It is readily executed, it requires less time, and the results afforded by it are most satisfactory. Finally, the separation of manganese from zinc, as described above, is of practical value.

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ON A COLORIMETRIC METHOD FOR THE ESTIMATION OF PHOSPHATES IN THE PRESENCE OF SILICA.¹

BY OSWALD SCHREINER.

Received July 29, 1903.

THE estimation of small amounts of phosphates in waters and aqueous extracts of soils and plants is a matter of daily occurrence in the study of field conditions of the soils, of surface and subsurface waters and growing crops, as carried on in the Bureau of Soils, U. S. Dept. of Agriculture. The method first used by Lepierre,² also by Jolles and Neurath,³ and perfected by Woodman and Cayvan,⁴ Veitch,⁵ and others, consisted in measuring the color developed by phosphates with ammonium molybdate in nitric acid solution against a known solution of phosphate as standard. As silica gives the same coloration with this reagent, its almost unfailing presence in natural waters is a disturbing factor. In the Woodman and Cayvan method, the silica is removed by evaporating once or twice to dryness with nitric acid and heating for two hours in an oven at 100°. The phosphate is then dissolved and separated from the insoluble silica by filtration, and estimated colorimetrically. The need of a more rapid field method induced Prof. F. H. King, Chief of the Division of Soil Management, to direct the investigation of silica and phosphate solutions, which has led to the method here reported.

In the method given in the following pages, the silica is estimated simultaneously with the phosphates. The method is based on the experimental observation that silica solutions will give different intensities of coloration under different conditions, while phosphates give the same coloration under these different con-

¹ Published by permission of the Secretary of Agriculture.

² *Bull. Soc. Chim.*, 18, 1213.

³ *Monatsh. Chem.*, 19, 5.

⁴ *This Journal*, 23, 96.

⁵ *Ibid.*, 23, 169.

ditions. When, as is usually done in the colorimetric estimation of phosphates, the nitric acid and ammonium molybdate solutions are added simultaneously to the silica solution, a certain intensity of color is developed. If, however, the ammonium molybdate reagent is added to the silica solution, and after a period of time the nitric acid, the intensity of color produced by the same amount of silica is far less than in the first case. Experiments have shown that the solution must stand at least one hour with the ammonium molybdate reagent before adding the nitric acid, in order to get the maximum effect. Some color is developed by the ammonium molybdate alone, but this is greatly influenced by the presence of other salts, temperature, etc., but on adding the nitric acid it always comes up to a definite intensity of color, which is approximately only one-half of the color developed when both reagents are added simultaneously. This different coloration of the silica solutions under these conditions is undoubtedly due to the formation of decidedly different silico-molybdates. Phosphates under these two conditions give exactly the same intensity of color.

REAGENTS.

(1) *Ammonium Molybdate Solution*.—Fifty grams of the pure salt in 1 liter of solution.

(2) *Nitric Acid* (sp. gr. 1.07).

(3) *Standard Phosphate Solution*.—0.5045 gram of pure, freshly crystallized sodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, is dissolved in water, 100 cc. of nitric acid (sp. gr. 1.07) added, and the whole diluted to 1 liter. The nitric acid is added to lessen the contamination with silica from the glass. One cc. = 0.0001 gram P_2O_5 .

(4) *Standard Colorimetric Solution*.—This is prepared by diluting 10 cc. of the above standard phosphate solution to about 80 cc. and then adding 9 cc. of nitric acid (sp. gr. 1.07), and 8 cc. of ammonium molybdate reagent and making up to 100 cc. After standing twenty minutes it is ready for use. Each cubic centimeter of this colorimetric solution is equal to 0.00001 gram P_2O_5 .

COLORIMETER.

The instrument used was similar to the one described and illustrated by Whitson.¹ It consists of a tube of colorless glass, 1 inch by 10 inches, with a side delivery tube near the bottom to connect by means of a rubber tube with a sliding reservoir for quickly changing the length of the standard colorimetric solution; a comparison tube, also of colorless glass and as nearly as practicable of the same dimensions as the measuring tube. It is provided with a 50 cc. and 100 cc. mark. The measuring tube is graduated so that one division of the scale is exactly equal to 0.01 of the distance between the bottom of the comparison tube and the 100 cc. mark. Both tubes have accurately ground and polished bottoms. The whole is mounted in a suitably constructed camera. A reflector of white paper, in place of the mirror of the Whitson instrument, at the top of the camera, illuminates the two solutions alike, while the images are viewed in a mirror below.

EQUIVALENCE OF THE SILICA COLORATIONS.

To determine the equivalence of the silica colorations, both an alkaline and a neutralized solution of silica were used. The first was prepared by dissolving silica in sufficient solution of sodium hydroxide, made by the action of sodium on water in a platinum dish, to make Na_2SiO_3 , and the second by dissolving crystallized Na_2SiO_3 in water and neutralizing with nitric acid. The strength of both solutions was accurately determined gravimetrically and then diluted.

EQUIVALENCE OF SiO_2 TO P_2O_5 WHEN BOTH REAGENTS ARE ADDED SIMULTANEOUSLY.

To 50 cc. of the silica solution, 5 cc. of nitric acid reagent and 4 cc. of ammonium molybdate reagent were added, and after twenty minutes compared with the standard colorimetric solution in the colorimeter. If the amount of color developed was too great for a safe reading, the solution was diluted and an aliquot part taken and read. The results are given in the following table:

¹ Bulletin 85, Wis. Agr. Expt. Station.

SOLUTION OF $\text{Na}_2\text{SiO}_3 + 2\text{HNO}_3$.

SiO_2 present. mg.	P_2O_5 required to equal color pro- duced by SiO_2 . mg.	1 mg. of P_2O_5 equals mg. of SiO_2 .
0.0826	0.1580	0.523
0.0826	0.1570	0.526
0.1652	0.3170	0.521
0.3303	0.6140	0.538
0.4139	0.7575	0.546
0.6606	1.2600	0.524
0.8258	1.5000	0.551
0.8258	1.5300	0.540

SOLUTION OF $\text{SiO}_2 + 2\text{NaOH}$.

0.0897	0.1835	0.489
0.3588	0.7220	0.497
0.8970	1.7350	0.517

Average, 0.525

EQUIVALENCE OF SiO_2 TO P_2O_5 WHEN THE AMMONIUM MOLYBDATE REAGENT IS ADDED ONE HOUR BEFORE THE NITRIC ACID.

To 50 cc. of the silica solution, 4 cc. of the ammonium molybdate reagent were added, and after standing one hour 5 cc. of the nitric acid reagent. After twenty minutes, readings were made as before. The results appear in the following table:

SOLUTION OF $\text{Na}_2\text{SiO}_3 + 2\text{HNO}_3$.

SiO_2 present. mg.	P_2O_5 required to equal color pro- duced by SiO_2 . mg.	1 mg. of P_2O_5 equals mg. of SiO_2 .
0.1652	0.1490	1.109
0.1652	0.1500	1.101
0.3303	0.3050	1.083
0.3303	0.3075	1.074
0.6606	0.5820	1.135
0.8258	0.7300	1.131

SOLUTION OF $\text{SiO}_2 + 2\text{NaOH}$.

0.0897	0.0900	0.997
0.3588	0.3500	1.025
0.8970	0.9075	0.988

Average, 1.071

RELATION BETWEEN THE TWO SiO_2 VALUES.

Examining the two silica values for each solution it will become apparent that one is approximately one-half the other. Taking the average value of each type this relation becomes

$$\frac{0.525}{1.071} = 0.49 \text{ or } \frac{1.071}{0.525} = 2.04.$$

The relation of the two silica colorations to each other is, therefore, for all practical purposes, one-half, and this value is used in the following equations for the method.

METHOD FOR THE DETERMINATION OF PHOSPHATES IN THE PRESENCE OF SILICATES.

On the different behavior of silica solutions towards ammonium molybdate under conditions which produce no change in the effect of this reagent on phosphates may be based a method for determining phosphates and silicates when both are present in a solution. There are in solution two unknown quantities; namely, silica (x) and phosphate (y). It has been shown that under a certain condition the silica gives a colorimetric reading which is only one-half as great as under another condition, whereas the phosphates give the same reading under either condition. Hence, when a solution containing both phosphates and silica is subjected to both these conditions, one reading will be obtained under one condition and another reading under the other condition, the differences in the readings being due entirely to the silica. There are, consequently, two equations, and having only two unknown quantities, these can be readily found. These two equations are:

$$(1) \ x + y = a,$$

$$(2) \ \frac{1}{2}x + y = b,$$

where (x) is the silica reading and (y) the phosphate reading, and (a) the experimental reading obtained under one condition, and (b) the experimental reading obtained under the other condition.

The working of this method is as follows:

Determination of the "a" Reading.—To 50 cc. of the solution add 5 cc. of nitric acid reagent and 4 cc. of ammonium molybdate reagent, and after twenty minutes the colorimetric reading is made. This gives the "a" reading in equation (1).

Determination of the "b" Reading.—To a second portion of 50 cc. of the solution add 4 cc. of ammonium molybdate solution and allow to stand one hour. At the end of this time add 5 cc. of nitric acid reagent and after twenty minutes read in the colorimeter. This gives the "b" reading in equation (2).

From these two readings the true phosphate (y) and silica (x) readings are readily calculated. The silica reading is twice the

difference between the "a" and "b" readings. To get the silica in milligrams of SiO_2 , multiply the reading by 0.00525. The phosphate reading is the difference between the "a" reading and the silica reading. To get the phosphate in milligrams of P_2O_5 , multiply by 0.01.

APPLICATIONS OF THE METHOD.

The method was tested on known solutions of phosphates in the presence of silicates. The results were as follows:

p. p. m. present.		Readings for 100 cc.		Readings for		p. p. m. found.	
SiO_2	P_2O_5	"a."	"b."	SiO_2	P_2O_5	SiO_2	P_2O_5
3.30	2.00	82.6	50.9	63.4	19.2	3.33	1.92
9.91	20.00	410.0	309.0	202.0	208.0	10.60	20.80

A known phosphate solution containing also the salts usually found in soil solutions or natural waters, silicates, sulphates, bicarbonates, chlorides, and nitrates was prepared and estimated.

p. p. m. present.		Readings for 100 cc.		Readings for		p. p. m. found.	
SiO_2	P_2O_5	"a."	"b."	SiO_2	P_2O_5	SiO_2	P_2O_5
3.30	2.00	85.0	52.0	66.0	19.0	3.46	1.90

The method was further tested on some standard salts which had been prepared for field investigations and contained known amounts of phosphates, besides silicates and other salts. These salts were dissolved in water and the solutions estimated. The results were:

No.	P_2O_5		p. p. m. of P_2O_5 in solution.		p. p. m. of SiO_2
	Present. mg.	Found. mg.	Present.	Found.	
1.....	0.535	0.536	10.70	10.72	4.18
2.....	0.520	0.532	10.40	10.64	4.65
3.....	0.550	0.522	11.00	10.44	4.26
4.....	0.468	0.471	9.36	9.42	3.70
5.....	0.480	0.451	9.60	9.02	4.04
6.....	0.525	0.506	10.50	10.12	4.26

The phosphates and silica in a well-water were determined. The amount of phosphates in proportion to the silica in this water is quite small, and its determination is, therefore, affected by the unavoidable error of reading. The results obtained with duplicates were as follows:

No.	Readings for 100 cc.		Readings for		p. p. m.	
	"a."	"b."	SiO_2	P_2O_5	SiO_2	P_2O_5
1.....	374.0	192.5	363.0	11.0	19.1	1.1
2.....	370.0	193.0	354.0	16.0	18.7	1.6
Average,					18.9	1.35

To this same well-water a known amount of phosphate was added and again estimated. The calculated p. p. m. of P_2O_5 is the sum of the p. p. m. added (10), and the average result obtained above (1.35).

No.	Readings for 100 cc.		Readings for		p. p. m. found.		p. p. m. calculated.	
	"a."	"b."	SiO ₂	P ₂ O ₅	SiO ₂	P ₂ O ₅	SiO ₂	P ₂ O ₅
1....	454	281	346	108	18.2	10.8	18.9	11.35
2....	455	285	340	115	17.9	11.5	18.9	11.35

A soil solution was prepared by washing 100 grams of soil with 500 cc. of water and filtering through a Chamberland filter. The resulting colorless solution was analyzed.

Reading for 100 cc.		Reading for		p. p. m.	
"a."	"b."	SiO ₂	P ₂ O ₅	SiO ₂	P ₂ O ₅
203	142	122	81	6.4	8.1

To this same soil solution 5 p. p. m. of P_2O_5 was added and again estimated.

Reading for 100 cc.		Reading for		p. p. m. found.		p. p. m. calculated.
"a."	"b."	SiO ₂	P ₂ O ₅	SiO ₂	P ₂ O ₅	P ₂ O ₅
254	192	124	130	6.5	13.0	13.1

A plant solution was prepared by washing 20 grams of corn plant with 500 cc. of water. The decolorization of the solution was effected by means of charcoal. The result found was as follows:

Reading for 100 cc.		Reading for		p. p. m.	
"a."	"b."	SiO ₂	P ₂ O ₅	SiO ₂	P ₂ O ₅
450	389	122	328	6.4	32.8

To this same plant solution a known amount of phosphates was added (10 p. p. m.) and the solution again estimated.

Reading for 100 cc.		Reading for		p. p. m. found.		p. p. m. calculated.	
"a."	"b."	SiO ₂	P ₂ O ₅	SiO ₂	P ₂ O ₅	SiO ₂	P ₂ O ₅
547	484	126	421	6.6	42.1	6.4	42.8

It is highly essential for these colorimetric tests that all plant and soil solutions be absolutely colorless.

THE DETERMINATION OF SMALL AMOUNTS OF POTASSIUM IN AQUEOUS SOLUTIONS.¹

BY F. K. CAMERON AND G. H. FAILYER.

Received August 13, 1903.

SOME years ago Morrell² offered a suggestion by which small quantities of potassium might be estimated. No experimental evidence was presented accompanying this suggestion, and so far as we are aware none has appeared elsewhere. Briefly, the method suggested is to separate the potassium from other bases in the form of the potassium platonic chloride, carefully free from an excess of reagents, take up in water and then add an 'excess of potassium iodide, when, on standing, a beautiful pink or rose color develops, which gradually deepens to a maximum intensity. By matching the intensity of the color against that which would be developed in a standard solution of known concentration, a measure of the amount of potassium present could be obtained. Qualitative tests indicated that the method could probably be so adapted as to have a great value for a class of work upon which we have been engaged for some time past, and consequently a quantitative examination of the method was undertaken. The color of the solution is due probably to the formation of a double salt of potassium iodide and platonic iodide or chloride, and is but indirectly a method for the detection or estimation of potassium, the same reaction being well known as a delicate one for the detection of small amounts of platinum in solution.

To test the accuracy with which the colors may be compared, a series of solutions of potassium platonic chloride was prepared containing the amounts indicated in the table, expressed in parts of potassium (K) in one million of solution.

TABLE I.

	a.	b.	c.	d.	e.	f.	g.
Calculated	0.16	0.31	0.62	0.94	1.40	2.03	2.81
Found	0.17	0.33	0.64	0.94	1.40	2.01	2.81

A portion of (g) diluted four times was used as a standard for comparison. An inspection of the figures indicates that the method is capable of a high degree of accuracy, the greatest divergence between the calculated and found amounts in this series

¹ Published by permission of the Secretary of Agriculture.

² This Journal, 2, 145 (1880).

being but one part in 50,000,000 parts of solution, although a percentage error slightly greater than 6 per cent. is involved. Nevertheless, considering the magnitude of the quantities involved, the result must be considered quite satisfactory.

A second series of solutions was prepared, the results of which are given in Table II in terms of potassium in 1,000,000 parts of solution.

TABLE II.

	a.	b.	c.	d.	e.	f.	g.
Calculated	0.175	0.35	0.70	1.05	1.57	2.28	3.15
Found.....	0.15	0.295	0.65	1.05	1.55	2.28	3.12

In this series, rather larger amounts of potassium iodide and of acid were used than in the first series, the results of which are given in Table I. The agreement between calculated and found results is not quite so happy in this case as in that recorded in Table I. The comparisons were made with much more difficulty, for the reason that the more dilute solutions showed a decided yellow tinge as compared with those of higher concentration. The cause for this will be discussed presently. Nevertheless it was decided to take solution *d* as the standard and make the determinations under the very adverse conditions obtaining. The results, while not as satisfactory as those presented in Table I, yet showed that the method could be used to give fairly satisfactory ideas as to the amounts of potassium in very dilute solutions, providing the separation of the potassium could be effected from other bases which form slightly soluble double chlorides with platinum. A seaching trial was then given the method, using solutions of potassium of known and of unknown strength, solutions of pure salt, and those containing the salts of other bases as well. Certain details of manipulation were found advisable and in some cases even essential to the successful use of the method, so that we feel justified in stating them here at some length.

If the solution under examination contain ammonium salts or organic matter, these must be removed, as the ammonia would precipitate a slightly soluble double chloride with platinic chloride, and the organic matter would color the solution and thus interfere with the reading. To effect their removal, the solution is evaporated with a few drops of sulphuric acid; enough to unite with all the bases presented. When dry, the residue is heated over a

naked flame, at first gently, then strongly. After cooling, a few drops of hydrochloric acid and of platinic chloride solution are added. The amount of these will depend upon the amount of residue. The platinum must, of course, be added in excess. This may be judged fairly well by observing whether the solution is yellow after any precipitate has settled out. The platinic chloride solution is run around over that portion of the dish containing the residue, a few drops of water, free from ammonia, being added if necessary. It is again evaporated to dryness on a water- or steam-bath. All operations after the ignition with sulphuric acid must be so conducted that no ammonia has access to the solutions. In the absence of ammonium salts and organic matter, the use of sulphuric acid may be dispensed with, the platinic chloride and a very small amount of hydrochloric acid being added to the original solution, one evaporation sufficing. When dry, or in the condition of a very stiff paste (but in the small quantities usually involved, the residue will be a thin layer over the bottom of the dish and may be carried to dryness) the dish is cooled, and the potassium platinic chloride washed, as described below. An excess of platinic chloride must have been used to throw down all the potassium, and as the color to be finally read is a measure of the platinum then present, it is obvious that all the forms of platinum other than potassium platinic chloride must be removed. To effect this with the solution of as little as possible of the precipitated potassium platinic chloride, we have used in our earlier work alcohol nearly saturated with this salt. Such a solution will only slowly dissolve the precipitate, and should a little of the alcohol evaporate, there will be no separation of potassium platinic chloride. We have washed and filtered through asbestos, resting on Witt or Hirsch plates fitted into carbon filters, using gentle suction. By this means the washing is done rapidly and there is a minimum evaporation of the alcohol containing potassium platinic chloride, if the suction be shut off as soon as the alcohol has passed through. The final washing is with ordinary strong alcohol, running through four or five small portions to remove the alcohol saturated with potassium platinic chloride. There is apparently a balancing of errors here, so that we have looked into this point very carefully, and have found that, while potassium platinic chloride has an easily measurable solubility in alcohol if the two are left in contact:

sufficiently long, yet this solubility is so small and takes place so slowly that in repeated experiments the alcohol used in washing the precipitate, as we have described above, would have no appreciable effect on the potassium platinic chloride in the precipitate. We have, therefore, abandoned the alcoholic solution of potassium platinic chloride, and wash the precipitate at once with six or eight small portions of 95 per cent. alcohol, being careful to remove each portion as completely as possible before the next one is added.

Should the alcohol have crept up the sides of the dish or funnel, carrying with it platinic chloride, any deposit of the latter must be carefully removed. After the washing is completed, the potassium platinic chloride is dissolved and washed through the asbestos with hot water into a flask, allowed to cool, a drop of concentrated hydrochloric acid is added, and then a solution containing potassium iodide until there is present a decided excess of this reagent. To secure the desirable tint of red, the color should be developed in a strong solution, and any necessary dilution be made some time (about four or more hours) later. It is, therefore, better not to dilute further than necessary in washing the potassium platinic chloride out of the filter before adding the hydrochloric acid and the potassium iodide.

In order to compare the test solutions with a standard, the procedure adopted is to place the solution under examination in a glass cylinder with a bottom ground flat and polished, such as the well-known apparatus used for determining ammonia by the Nessler method. A second cylinder with precisely the same dimensions as the first, but made with a side arm at the bottom, contains the standard solution. Both cylinders are clamped into position parallel with each other, within a box or camera¹ fitted with mirrors, so that a beam of light can be thrown through the cylinders from above and the images of their cross-sections be seen on a lower mirror arranged at a convenient angle. The bottoms of the cylinders rest upon a shelf with orifices so arranged that no light from the upper mirror falls upon the lower mirror other than that which passes through the columns of liquid contained in the cylinders. By means of the side arm and rubber tubing, the cylinder containing the standard solution

¹ A convenient form of instrument for this purpose is that described by Whitson, Bull. No. 85, Wis. Agr. Expt. Station.

is connected with a movable reservoir outside the camera which can be raised or lowered at will, thus regulating the depth of the standard solution within the cylinder. This depth of the standard solution is adjusted until the intensity of color of the two images is the same. The cylinder containing the standard solution is fitted with a scale, for which purpose a strip of cross-section paper pasted along the side answers very well, and is then calibrated on the assumption that when the images given in the camera by two solutions contained in identical cylinders are the same, the concentrations of the two solutions are inversely proportional to the height of the two columns of liquid. This assumption is not free from objections on theoretical grounds, but has been found entirely justifiable in the case here considered, as the result of long and repeated series of experiments. It carries with it as a necessary consequence the further assumption that the color produced by the solution in a standard cylinder is dependent only upon the amount of coloring-matter present and not upon the amount of water, a point of importance, since it enables one to avoid having always to dilute the test solution to mark in the cylinder, which procedure might sometimes be undesirable, as the following pages will show.

The substance which causes the red color in these solutions has not been determined. An inspection of the literature describing the double halides of platinum and potassium failed to give any positive information, and we have not felt justified at the present time in extending our investigation so as to definitely decide this question. In order to obtain some idea as to the proportions of the reagents necessary to the use of the method, a series of experiments was made.

For this purpose ten solutions were prepared, each containing the same amount of potassium platonic chloride, this salt being used instead of platonic chloride, since it is possible to weigh the desired amount of platinum more accurately with the former than with the latter salt. And since there was no purpose of studying the relation of the solution to solid phases, they were in all cases, after the addition of potassium iodide, brought to a volume of about 50 cc., enough to have no solid phase present at the beginning of the experiments. In each solution there was brought the amounts of potassium iodide indicated in the table. The ratios are approximate only.

TABLE III.

Weight of K_2PtCl_6 taken. mg.	Weight of KI required to form K_2PtI_6 . mg.	Weight of KI used. mg.	Ratio of KI used to that required to form K_2PtI_6 .	Remarks.
a...3.105	6.26	1.093	0.2 : 1	Pink, soon darkened, the pink color disappeared and a black residue separated out.
b...3.105	6.26	2.395	0.33 : 1	
c...3.105	6.26	3.975	0.66 : 1	
d...3.105	6.26	7.95	1.25 : 1	Pink; turned dark after a time; black residue.
e...3.105	6.26	15.9	2.5 : 1	Pink; shining metallic film.
f...3.105	6.26	31.8	5 : 1	Pink.
g...3.105	6.26	47.7	7.5 : 1	"
h...3.105	6.26	63.6	10 : 1	"
i...3.105	6.26	79.5	12.5 : 1	"
k...3.105	6.26	95.4	15 : 1	"

Solutions(e) to (k) inclusive, were of a satisfactory pink or red color, which apparently remained permanent for seven days. A very careful examination with starch paste at the end of that time yielded a faint reaction for iodine in some of the solutions, and the experiments were then abandoned. The results showed that it would be desirable to use about five times the amount of potassium iodide required by calculation to form the salt of the formula K_2PtI_6 , but that no obvious advantage was produced by having a larger excess present.

It early developed in the work that the color of the solution did not reach a maximum until some hours after the reagents were brought together, and that the speed of the reaction was greatly augmented by the presence of a little free acid.¹ Therefore, a series of solutions were prepared from one containing about two parts per million of potassium to which the two drops of the acids indicated were added, the acids being taken from the ordinary reagent bottles of the laboratory shelf and marked "concentrated." Readings were made in the times indicated, a solution whose strength was known approximately (but not accurately), and in which the rose color had been developed twenty-four hours previously being used as the standard.

¹ It is obvious that the amount of free acid permissible is very small, otherwise iodine would be liberated.

TABLE IV.

Acid used.	After 1 hour.	After 1½ hours.	After 4¼ hours.	After 22 hours.
No acid.....	{ Trace Trace	{ Trace Trace	{ Lost 0.20	{ ... 0.33
Hydrochloric.....	{ 1.33 1.33	{ 1.53 1.56	{ 1.93 1.86	{ 1.93 1.93
Acetic	{ 0.46 0.53	{ 1.13 1.13	{ 1.83 1.80	{ 1.86 1.86
Nitric.....	{ 1.33 1.26	{ 1.53 1.53	{ 1.73 1.80	{ 1.86 1.86
Sulphuric	{ 1.33 1.33	{ 1.56 1.60	{ 1.86 1.93	{ 1.93 2.00

The results of these experiments, with many others which it is not worth while recording here, have led us to the procedure of adding one drop of strong hydrochloric acid to the solution before adding potassium iodide and then waiting at least four hours for a full development of the color before reading in the colorimeter. It has, moreover, been found desirable to make all dilutions, even of strongly colored solutions, at least one hour before readings are taken. The pink color can be brought to its maximum intensity within a comparatively few minutes, by warming the solution, and this procedure we occasionally follow rather than the one just advised. But unless great care has been taken to eliminate all traces of alcohol before dissolving the precipitate from the alcohol, warming the solution is apt to produce a yellowish or brownish tinge in the pink color, rendering its comparison with the standard much more difficult, if not impossible.

To test the efficiency of the method when other bases than potassium are present, a series of experiments were made, the results of which are given in the following table. Since becoming more expert in handling the method, we generally obtain more satisfactory results than these, but we give them here as actually obtained when working out the method, as indicating the probable order of accuracy to be expected by one having no previous experience with the method. Except as otherwise indicated, all results are expressed in this paper as parts per million of solution.

TABLE V.

Calculated.	Found.	Remarks.
50	52.7	50 parts Na, 50 parts Mg, and 50 parts Ca per 1,000,000 parts solution, also present.
	48.0	
	48.0	
	53.5	
	52.7	

20	19.8	}	20 parts Na, 20 parts Mg, and 20 parts Ca per 1,000,000 parts solution, also present.
	19.4		
	20.2		
	21.0		
5	19.4	}	5 parts Na, 5 parts Mg, and 5 parts Ca per 1,000,000 parts solution, also present.
	6.4		
	6.4		
	6.9		
20	6.0	}	No other base present.
	20.2		
	20.1		
	20.1		
	20.0	}	Aqueous extract of a soil.
	12.2		
	11.9		
	11.2		
	11.5	}	" " " "
	30.6		
	30.2	}	" " " "
	20.3		
	24.3	}	" " " "
	9.7		
	9.3	}	" " " "
	12.7		
	13.8	}	" " " "
	58.0		
	61.0	}	" " " "
	13.0		
	14.5	}	" " " "

To test the method still further, the three solutions cited above and containing sodium, magnesium and calcium, as well as potassium, were further examined, comparisons being made with solutions containing 2 parts and 3 parts per million of potassium, respectively, and the potassium being estimated gravimetrically as well, according to the well-known method of weighing the precipitated potassium platonic chloride, large volumes of the solutions being taken for this purpose. The results have been tabulated as follows:

TABLE VI.

Calculated.	Gravimetric.	Standard 2 parts per million.	Standard 3 parts per million.
5	{ 4.7	5.2	5.3
	{ 4.2	5.2	5.3
20	{ ..	20.5	20.4
	{ 22.5	20.5	20.4
50	{ 50.7	49.0	48.8
	{ ...	48.5	48.8

These results show that the method can be regarded as fairly satisfactory, even when relatively large proportions of other bases are present. The method has been used successfully with solutions containing originally as much as 400 parts per million of potassium, by properly diluting. But we do not advise its application to solutions containing more than 50 parts per million of this base, at most, unless the volume at command is so small as to prevent obtaining a sufficiently large precipitate to weigh satisfactorily. The method seems to be most satisfactory when applied to solutions containing from 1 to 10 parts per million of the base, and on the whole the most satisfactory concentration for the standard we have found to be 2 parts per million. For solutions containing less than 2 parts per million, the method has been found quite satisfactory, if care be exercised. The weak point of the method is obviously the handling and washing of the precipitate of potassium platonic chloride, and the smaller this is, the greater the difficulty becomes, and in consequence the greater the care which must be exercised.

Attention has been called above to the fact that the solutions to which the potassium iodide had been added were sometimes brownish or yellowish, thus rendering their comparison with others impossible or at least unsatisfactory. The cause of this escaped us for some time. But the fact that the pink color is not produced when potassium iodide is added to an alcoholic solution of platonic chloride, led Mr. J. F. Breazeale, of this laboratory, to suspect that small quantities of alcohol left in the filter, when washing the potassium platonic chloride free from other salts, and subsequently brought into the solution on the addition of hot water, might be responsible for the trouble. Experiments have amply verified this view. The addition of small amounts of alcohol to aqueous solutions in which the pink color had already been developed, invariably turned them yellow. This change to yellow was found to take place more rapidly in the sunlight. If the solution containing the platinum salt and to which the potassium iodide has been added together with a little alcohol, be heated, the pink color first appears, develops very rapidly, but always with a yellowish or brownish tinge, and after a few minutes turns to a clear yellow. The presence of a free acid retards the development of the yellow color, and if this color be desired in the first place,

acid should preferably not be added. The yellow color is not so intense as the pink we have been describing, but much stronger than the yellow obtained from an equivalent amount of platinum combined as platinic chloride. We have, therefore, examined it with a view to its application for the quantitative estimation of platinum and indirectly of potassium.

A series of solutions containing known amounts of potassium was prepared. Mr. Breazeale and Mr. J. G. Smith, of this laboratory, were requested to read them independently against standards prepared by themselves, developing first the pink color and then subsequently developing the yellow color in the identical solutions which had just been read, and then re-reading. The results obtained follow under the headings B and S.

TABLE VII.

Calculated.	Found by B.		Found by S.	
	Pink.	Yellow.	Pink.	Yellow.
0.75	0.80	0.84	0.70	0.80
1.25	1.20	1.26	1.10	1.30
1.25	1.20	1.34	1.30	1.30
2.50	2.48	2.62	2.40	2.40
2.50	2.48	2.52	2.40	2.40
3.75	4.44	3.40	4.00	3.80
5.00	...	5.30
5.00	...	5.10
10.00	...	10.00
10.00	..	10.00

A series of water extracts of soils was then prepared, in which other bases than potassium would also be present, and they were compared by means of both the pink and the yellow color methods. The results follow:

TABLE VIII.

Pink.	Yellow.
2.4	2.8
12.5	13.5
4.2	4.4
17.7	17.1
5.7	5.4
18.8	18.9
23.9	26.2
4.4	4.7

From the results it would appear that the yellowish color can be used as well as the pink over the range of concentrations indicated

in these tables. The yellow color is probably somewhat easier to "match" than the pink, and its use is advised when the higher concentrations are concerned. It is also of considerable advantage in that it affords a ready check upon the determination by the pink color, a matter of importance when such small amounts of unknown solutions are available as to preclude duplicate determinations. The yellow color is not so deep or strong, however, as the pink, and for this reason the latter is much more advantageous than the former, when high dilutions are concerned.

From what has been presented in this paper, it is evident that we have here a very sensitive method, susceptible of a high degree of accuracy, for determining quantitatively minute quantities of potassium. No unusual apparatus or skill is required for its manipulation. But it will only yield satisfactory results when care is exercised, and especially in the handling and washing of the small precipitate of potassium platonic chloride. The limit of dilution to which the method is applicable is probably much higher than the figures given here would indicate, but we have not attempted to determine this limit, and are not prepared to make a more definite statement concerning it.

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THE ESTIMATION OF TITANIUM.

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Received August 17, 1903.

OF THE many elements which present themselves for determination to the metallurgical chemist of to-day, there are a select few which have won for themselves a reputation based upon the tediousness or the difficulty of the preliminary separation from other constituents which may be present. In this class of unenviable reputation we may place the element titanium for, although its determination presents no difficulties to the experienced chemist with time at his disposal, his less fortunate brother, at the same task in the rush of a works laboratory, is apt to find that either speed or accuracy must be sacrificed in answer to the demands made on him.

For three-quarters of a century the estimation of this element

in all pure solutions involved six or eight hours' boiling, an operation which had often to be repeated, or else a tedious treatment with ammonium sulphide, until Gooch¹ discovered that titanium could be precipitated quantitatively in a convenient form by a few minutes' boiling, and Blair² added to this a modification which permitted a much more rapid separation from iron than heretofore. Thus the determination became comparatively easy, but nevertheless under the pressure of heavy work and insufficient time, the demand for a shorter method has become noticeable and in response several modified processes have appeared in the chemical literature of the day. To inquire into the accuracy of these was the first object of the following investigation. At the same time it has not been considered necessary to confine the attention to speed, and hence some experiments have been incorporated simply because they have a bearing upon the estimation of titanium in general. In the foregoing statements, there has been a reservation regarding Weller's³ excellent colorimetric method; it is rapid and accurate, but unfortunately is only adapted for the estimation of small quantities of titanium.

To the chemist engaged in the analysis of minerals and rocks, the separation of titanium from some of the rarer elements such as zirconium or vanadium is a matter demanding attention, but to the metallurgical chemist who meets these more uncommon elements either rarely or in minute quantities, the elimination of iron, aluminum and phosphorus is usually the only problem to be considered. For this reason, the behavior of these last three elements, with the one under consideration, has been the object of this study. At the same time it will readily be seen that all our present knowledge can be directly employed in the final stages of any of the methods investigated.

Without referring in detail to the modifications of the older processes, descriptions of which are to be found in modern chemical or metallurgical journals, it is proposed to discuss the merits of three methods which are apparently new in principle. In the following pages, these have been designated for convenience by the author's name; if any injustice has been done, the writer begs to offer his apologies.

¹ Gooch: Bull. 27, U. S. Geol. Survey, p. 16; *Proc. Am. Acad. Arts Sci.*, n. s., 12, 435; *Chem. News*, 72, 55, 68.

² Blair's "Analysis of Iron and Steel," 4th edition, p. 179.

³ *Ber. d. chem. Ges.*, 18, 2593.

For the purpose of the investigation a solution of pure titanium dioxide was necessary, and this was prepared from rutile by Wöhler's¹ method. The mineral at hand, however, was very impure and only a small yield of potassium fluotitanite was obtained. The process was therefore modified by preparing, according to the directions of Streit and Franz,² a quantity of fairly pure titanium dioxide, which was then converted into the fluotitanate and finally by the action of strong sulphuric acid into titanium sulphate. Incidentally it may be mentioned that this modification is much more convenient for the preparation of considerable quantities of pure potassium fluotitanate, but Merz's³ process, a description of which was found after the preparation had been made, appears to be the best. After the removal of the excess of sulphuric acid, the pasty mass of potassium and titanium sulphates was treated with water, solution being accelerated by warming to 70° C. and agitating with a blast of air. After suitable dilution, ammonia was added to weighed quantities of this standard solution till alkaline, followed by acetic acid in decided excess⁴ and the titanium dioxide, precipitated by boiling for two or three minutes, was filtered off, thoroughly washed, and ignited to constant weight.

Weight of solution. Grams.	TiO ₂ found. Gram.	TiO ₂ in 25 grams standard solution. Gram.
27.8603	0.2611	0.2343
27.8518	0.2624	0.2355
27.8384	0.2624	0.2356
27.8540	0.2620	0.2351

Mean value = 0.2351

Every precaution was taken to make these results as accurate as possible, and it is believed that the mean approximates very closely to the true value.

BASKERVILLE'S METHOD.

The detailed description⁵ may be briefly summarized as follows: The material is fused with potassium bisulphate and the mass dissolved in water, ammonia is added till alkaline, and the hy-

¹ Wöhler: *Am. Chem. Pharm.*, 74, 212.

² Streit and Franz: *J. prakt. Chem.*, 108, 65; *Ztschr. Chem.* [2], 6, 256.

³ Merz: *J. prakt. Chem.*, 99, 157.

⁴ Gooch: *Loc. cit.*

⁵ Baskerville: *J. Soc. Chem. Ind.*, 19, 419; also this Journal, 16, 427.

dioxides are filtered off, washed and redissolved in hydrochloric acid. Ammonia is then added till the solution reaches the so-called neutral point and the volume is brought to about 100 cc., sulphur dioxide is passed in to saturation, and three minutes' boiling precipitates the titanium dioxide. If the latter be not perfectly white, the process is repeated. One point deserves attention. After dissolving the hydroxide precipitated by ammonia in 15 cc. of dilute hydrochloric acid, to quote the original: "Very dilute ammonium hydroxide is now added slowly to neutralize the acid. When a slight permanent precipitate is obtained, 1 per cent. hydrochloric acid is added drop by drop, boiling after each addition until the solution just becomes clear; the total amount of liquid should not be more than 100 cc." The writer has endeavored to follow out these directions in a number of cases, but has always failed to secure the desired effect. The 1 per cent. hydrochloric acid will not dissolve the precipitate even after a large quantity has been added, and this result could be predicted from a knowledge of the behavior of salts of titanium in solution. For example, a solution containing titanium and ferric chlorides, after being nearly neutralized, but while still free from the faintest trace of a precipitate, becomes turbid on boiling, and the metatitanic acid thus precipitated is apparently quite unattacked by 1 per cent. hydrochloric acid even in considerable amount. The following modification was, therefore, adopted in the experiments to be described: Dilute ammonia was added to the solution of the chlorides until a faint permanent precipitate was formed which was just redissolved with a drop or two of dilute hydrochloric acid, or in other words, the solution was treated exactly as though a basic acetate separation were to be made. In all other details the method was carefully followed, notwithstanding the fact that slight alterations suggested themselves from time to time.

The Separation of Titanium from Iron.—Iron is almost invariably present in the materials in which titanium is to be estimated, and consequently this separation was the first to be studied. To a weighed quantity of the standard solution, 0.5 gram iron as $\text{Fe}_2(\text{SO}_4)_3$ was added, then ammonia to alkalinity, followed by acetic acid in slight excess. The latter reagent was employed because it was thought that traces of titanium, which might have escaped precipitation with ammonia alone, would then be thrown

down, although no direct experiments were made to settle the point. It will be remembered, however, that Gooch found advantageous the presence of a distinct excess of acetic acid when estimating titanium in a pure solution. The hydroxides, after washing till the sulphates were almost entirely removed, were dissolved in dilute hydrochloric acid, and the solution neutralized with ammonia till a faint permanent precipitate was formed, which was redissolved in a drop or two of dilute acid. Sulphur dioxide was then passed in to saturation; in the course of a few minutes a white precipitate usually began to form. After boiling for five minutes the hydrated titanium dioxide separated out in flocks, and the supernatant liquid showed the characteristic, faint greenish tinge of solutions containing ferrous chloride. The precipitate was filtered off, washed with hot water, and ignited to constant weight.

	Weight of solution. Grams.	TiO ₂ found. (I) Gram.	TiO ₂ by standard. Gram.	Error.
(3)	6.639	0.0662	0.0624	0.0038+
(4)	7.720	0.0707	0.0684	0.0023+
(5)	11.169	0.1136	0.1050	0.0086+
(6)	11.167	0.1138	0.1050	0.0088+
(7)	11.085	not	0.1045
(8)	11.087	weighed.	0.1045
(9)	11.137	0.1062	0.1049	0.0013+
(10)	11.140	0.1108	0.1049	0.0059+

As will readily be understood, the amount of iron thrown down with the titanium dioxide depends on the manner in which the solution is neutralized. Where this was carried out with the greatest care, the solution being only gently warmed till completely reduced, as was the case in (4) and (9), the results approximated to the truth with exactness sufficient, at least, for technical work; this accuracy is, however, due to a balancing of errors, as will be shown later on. Numbers (7) and (8) were treated with ammonia till a faint precipitate remained persistently; on heating, the turbidity appeared to become less, and before 100° C. had been reached, the burner was removed and sulphur dioxide passed in. The first few bubbles produced a reddish white precipitate; after saturation and boiling, this turned brownish red in color and evidently contained a considerable quantity of iron. This became more apparent on ignition and no weighings were made at this stage. The purity of the titanium dioxide may be

judged roughly from its color after precipitation; if snow-white, iron is almost entirely absent, but when contaminated with that element, a reddish or pinkish tinge is noticeable, the more pronounced the greater the impurity. The same effects may also be noted in the ignited precipitate. The precipitates were dissolved, if very impure, by treatment with potassium bisulphate, or otherwise by fusion with sodium carbonate and solution in concentrated sulphuric acid; in the former case, care was taken to remove from the solution subsequently obtained, the platinum from the crucible. The entire process as described above was then repeated, yielding the following results:

	Weight of solution. Grams.	TiO ₂ found. (II) Gram.	TiO ₂ by standard. Gram.	Error.
(3)	6.639	0.0580	0.0624	0.0044—
(4)	7.270	0.0651	0.0684	0.0033—
(5)	11.169	0.1032	0.1050	0.0018—
(6)	11.167	0.1031	0.1050	0.0019—
(7)	11.085	0.1056	0.1045	0.0011+
(8)	11.087	0.1027	0.1045	0.0018—
(9)	11.137	0.1012	0.1049	0.0037—
(10)	11.140	0.1025	0.1049	0.0024—

Some of these precipitates still retained iron and the results should be corrected before criticism is made; determinations were not carried out in (3) and (4), and in (6), which was accidentally lost after estimating the platinum iron was also present, and the error is greater than —0.0019 gram.

	TiO ₂ found. (II) Gram.	Fe ₂ O ₃ # therein. Gram.	TiO ₂ -Fe ₂ O ₃ . Gram.	TiO ₂ by standard. Gram.	Error.
(5)	0.1032	0.0027	0.1005	0.1050	0.0045—
(7)	0.1056	0.0015	0.1041	0.1045	0.0004—
(8)	0.1027	0.0001	0.1026	0.1045	0.0019—
(9)	0.1012	0.0002	0.1010	0.1049	0.0039—
(10)	0.1025	0.0000	0.1025	0.1049	0.0024—

From these results, some interesting deductions can be drawn. In the first place, it will be remembered that in (7) and (8) so much iron was thrown down in the first precipitation that the weighing was omitted, and it will be seen that in these two instances the final errors are the lowest of all. One might therefore purposely produce a similar condition with a view of attaining greater accuracy. Again it will be observed that, presumably, after experience in the operation had been gained, the second

precipitation yielded titanium dioxide practically free from iron, as shown in (8), (9), and (10), but apparently always at the expense of a loss in the titanium. Omitting (7) as exceptional, the average loss in the element under estimation is 3 per cent. In most of the filtrates, colorimetric estimations were made of the titanium which remained in solution, but no light was thrown upon the question as to the conditions under which the greatest loss took place. The amounts found varied from traces to 1.5 milligrams.

From the standpoint of technical work, the uncorrected results of the second precipitation are worth noting. The errors here can be overlooked in view of the fact that titanium is not bought and sold at so much per unit, and if a small amount of iron remain in the final precipitate it serves but to balance the loss in the element estimated. An interesting case may be cited at this point as an instance of the curiously exact results which may sometimes be obtained in cases in which all precautions are not taken. The impure titanium dioxide obtained in the first precipitation in (5) and (6) was fused with potassium bisulphate, and inadvertently the second precipitation was made without removing the platinum by hydrogen sulphide as usual. After weighing, the precipitates were fused again with potassium bisulphate in porcelain and the platinum and iron estimated; in (6), an accident prevented the completion of this operation after the platinum, which amounted to 0.0019 gram, had been determined.

	TiO ₂ by standard. Gram.	TiO ₂ found. Gram.	TiO ₂ found less impurities. Gram.
(5)	0.1050	0.1059	0.1005
(6)	0.1050	0.1050	0.1031 (less Pt only.)

It may be remarked at this point that Baskerville makes no provision for the removal of the platinum which is always present after a fusion with potassium bisulphate and that this precaution may only be neglected in the hope that a balancing of errors will ensue.

The Separation of Titanium and Aluminum.—To weighed quantities of the standard solution were added 1.75-gram portions of alum, equivalent to 0.1877 gram alumina. The hydroxides were precipitated with ammonia, washed, redissolved in hydrochloric acid, the solution neutralized with ammonia and after dilution to 100 cc., boiled for three minutes.

	Weight of solution. Grams.	TiO ₂ found. (I) Gram.	TiO ₂ by standard. Gram.	Error.
(11)	6.105	0.0575	0.0574	0.0001+
(12)	6.215	0.0592	0.0584	0.0008+
(13)	11.185	0.1076	0.1052	0.0024+
(14)	11.177	0.1044	0.1052	0.0008—

To ascertain what quantity of alumina still remained in these precipitates, recourse was had to Gooch's method which assured the separation of the small amount retained without the risk of losing any of the titanium. The precipitates were accordingly fused with pure sodium carbonate, leached with water, re-fused with sodium carbonate and treated with concentrated sulphuric acid until complete solution took place. The remaining steps of the process were carried out as usual, the titanium being precipitated from a solution strongly acidified with acetic acid. After this treatment the following results were obtained:

	Weight of solution. Grams.	TiO ₂ found. (II) Gram.	TiO ₂ by standard. Gram.	Error.
(11)	6.105	0.0574
(12)	6.215	0.0582	0.0584	0.0002—
(13)	11.185	0.1044	0.1052	0.0008—
(14)	11.177	0.1036	0.1052	0.0016—

It will thus be seen that with the smaller amounts of titanium in (11) and (12), the separation from a fairly large quantity of alumina is remarkably sharp for one precipitation, much more so than in any of the cases given by Gooch as examples of the efficiency of his method. Even the larger quantities of titanium dioxide retain only trifling quantities of alumina, and it is easy to arrange for their removal. Having regard to the observation which has been made in the course of this study that minute but determinable quantities of titanium are almost invariably to be found in the filtrates from Baskerville's method, but very much smaller quantities or only traces in the filtrates from Gooch's method, and desiring to avoid loss as far as possible, the following would appear to be the best method of purification. The impure titanium dioxide is fused with pure sodium carbonate, leached with water, re-fused with sodium carbonate, and the melt dissolved in concentrated sulphuric acid by gentle warming; the titanium dioxide in this solution is then precipitated according to Gooch's directions.

The Separation of Titanium and Phosphorus.—The fact that

titanium phosphate is almost insoluble in dilute hydrochloric acid would lead to the prediction that a separation of these elements under the conditions laid down by Baskerville could not be expected, and consequently no experiments were made in this direction. A little later, however, some evidence bearing on this point will be presented.

The Separation of Titanium from Iron, Aluminum and Phosphorus.—Since these elements present themselves in varying quantities in nearly every instance in which titanium is to be estimated, an inquiry was made as to their behavior when all are present at the same time. The following quantities were taken:

Standard solution of TiO_2	10 cc.
50 cc. solution of $\text{Fe}_2(\text{SO}_4)_3$	= 0.5000 gram Fe.
0.9294 gram alum	= 0.1000 gram Al_2O_3 .
0.1000 gram sodium phosphate	= 0.0200 gram P_2O_5 .

After diluting to 200 cc., ammonia and acetic acid were added as already described and the precipitate, after washing, was re-dissolved in hydrochloric acid, 1:1. Some flocks of titanium phosphate, which obstinately resisted attack, were digested with concentrated hydrochloric acid, in which they finally dissolved. The solution was then neutralized and boiled for five minutes after saturating with sulphur dioxide. The color of the precipitated titanium dioxide varied from almost pure white to gray or brownish, and a considerable amount of impurity was present in each case, as may be seen from the following:

	Weight of solution. Grams.	TiO_2 found. (I) Gram.	TiO_2 by standard. Gram.	Error.
(15)	11.180	0.1464	0.1052	0.0412+
(16)	11.174	0.1274	0.1052	0.0222+
(17)	11.210	0.1316	0.1055	0.0261+
(18)	11.209	0.1256	0.1055	0.0201+

The precipitates were accordingly fused with sodium carbonate, dissolved by gently warming with strong sulphuric acid—the solution in this and similar instances was often incomplete, necessitating filtration and re-fusion—and after suitable dilution, precipitated with ammonia. Finally, a reprecipitation was made in the neutralized chloride solution, as described above, yielding the results stated below.

	Weight of solution. Grams.	TiO_2 found. (II) Gram.	TiO_2 by standard. Gram.	Error.
(15)	11.180	0.1105	0.1052	0.0053+
(16)	11.174	0.1154	0.1052	0.0102+
(17)	11.210	0.1203	0.1055	0.0148+
(18)	11.209	0.1127	0.1055	0.0072+

Thus a double precipitation in a neutralized chloride solution fails to effect the complete separation of the titanium from the elements associated with it in this instance. It remained, then, to discover what amount of pure titanium dioxide was present in these precipitates and whether any one element was responsible for the magnitude of the error.

The precipitates were fused with sodium carbonate, leached with water, and re-fused with the same material. The mass was then dissolved in concentrated sulphuric acid with the aid of gentle heat and after pouring into water, in (15) and (16) hydrogen sulphide was passed in to saturation in order to discover whether appreciable amounts of platinum were present, an element which is well known to contaminate titanium dioxide, if present during its precipitation; only traces were found and the question was considered as settled. After carefully adding ammonia till just alkaline, a quantity of dilute sulphuric acid equivalent to 2.5 grams of the pure acid was added, then 20 grams sodium acetate and sufficient acetic acid to make 11 per cent. absolute acid in the solution. If ferric iron could be detected, sulphur dioxide was passed in at an appropriate stage. After boiling for three minutes and digesting on the water-bath for half an hour, the titanium dioxide was filtered off and washed with 7 per cent. acetic acid.

	Weight of solution. Grams.	TiO ₂ found. (III) Gram.	TiO ₂ by standard. Gram.	Error.
(15)	11.180	0.0948	0.1052	0.0104—
(16)	11.174	0.0976	0.1052	0.0076—
(17)	11.210	0.1010	0.1055	0.0045—
(18)	11.209	0.0968	0.1055	0.0087—

These precipitates still retained trifling quantities of iron.

With regard to the disturbing factor, some evidence may be given. After fusing 0.1105 gram of impure titanium dioxide obtained in the second precipitation in neutralized chloride solution in (15), with sodium carbonate and leaching with water, the phosphorus was determined in the extract and found to be equivalent to 0.0123 gram phosphorus pentoxide; the final precipitate from the acetic acid solution in the same instance weighed 0.0948 gram. $0.1105 - 0.0123 = 0.0982$ gram impure TiO_2 — P_2O_5 .

Any alumina would, of course, have been removed with the

phosphorus, but, judging from the separation previously studied, there was now but a minute amount present and the difference $0.0982 - 0.0948 = 0.0034$ gram represents in all probability the iron eliminated, the latter clearly being indicated in the waste liquors by qualitative tests. Similar treatment of the titanium dioxide obtained in the second precipitation in the neutralized chloride solution in (17) and (18) revealed the fact that phosphorus constitutes almost the entire impurity, with a small quantity of iron as its associate. In the filtrates from the neutralized chloride separations, titanium was found regularly and in amounts varying from traces to 3 or even 4 milligrams.

While, obviously, the attempted separation is rendered practically valueless by such serious losses in titanium, it must not be forgotten that the object was to subject the method to a severe test. The presence of the titanium phosphate no doubt made difficult the adjustment of the acidity of the solution, since it would be precipitated by the ammonia in neutralizing, and, dissolving very slowly or not at all, would induce the belief that but little free acid remained. Consequently the removal of the phosphorus and at the same time the remaining aluminum, after the first precipitation, by fusing with sodium carbonate and leaching with water should be undertaken, after which the problem resolves itself into the separation of iron and titanium, which has already been studied. Also, if a fusion with potassium bisulphate has been made at any stage, the platinum, which is invariably present, should be removed, preferably in hot sulphuric acid solution, before the final precipitation.

Brakes¹ has modified Baskerville's method by replacing the potassium bisulphate, used in the preliminary fusion, by sodium and potassium carbonates. The melt is dissolved in dilute hydrochloric acid, and, after filtering, the titanium is precipitated in the neutralized chloride solution as usual. Some results are given showing that closely agreeing figures may be obtained, but one cannot gather what degree of accuracy is reached.

ARNOLD'S METHOD.

Blair's statement that "when a solution of ferric chloride containing titanic and phosphoric acids is evaporated to dryness, a compound of titanic acid, phosphoric acid and ferric oxide is

¹ Brakes: *J. Soc. Chem. Ind.*, 18, 1097.

formed, completely insoluble in dilute hydrochloric acid,"¹ suggests a method of removing, with comparative ease and certainty, the large amount of iron and alumina which have usually to be separated from titanium in analytical work. Morgan² and Arnold³ have published methods founded upon this observation, and an inquiry was made as to their value. Waterhouse⁴ indeed states that the results may not be accurate, but presents no evidence in support of his assertion.

The descriptions may be abbreviated as follows: The finely ground ore, to which has been added 1 gram of ammonium phosphate, is treated with concentrated hydrochloric acid, the solution evaporated to dryness and baked for some time, then treated with dilute hydrochloric acid and the residue filtered off, the filtrate being discarded. By fusing with sodium carbonate and leaching with water, the phosphorus and most of the silica and alumina are removed; the insoluble sodium titanate is brought into solution by treatment with potassium bisulphate, and the titanium dioxide precipitated from an acetic acid solution as described by Gooch. The crucial point is the insolubility of the phosphotitanate of iron in dilute hydrochloric acid, and neither of the authors specify the strength of the acid to be employed. In the descriptions which follow, the words "per cent." denote the parts by weight of anhydrous hydrochloric acid per 100 grams of solution.

The experiments were carried out in the following manner: A portion of the standard titanium dioxide solution was taken, and 0.5 gram iron as $\text{Fe}_2(\text{SO}_4)_3$ added; the hydroxides, precipitated by ammonia and a slight excess of acetic acid, were washed and dissolved in hydrochloric acid, and, after the addition of 1 gram of ammonium phosphate, the solution was evaporated to dryness and baked at the highest temperature of the hot plate for seven hours. To ascertain approximately the temperature to which the material was exposed, a thermometer was placed in an empty beaker on the same spot on the hot plate and left for some hours; the highest temperature reached was 180°C . The cooled mass was then digested with 0.4 per cent. hydrochloric acid for some hours at a temperature of about 100°C ., but no action of any

¹ Blair's "Analysis of Iron and Steel," 4th edition, p. 85.

² Morgan: *Chemical News*, 78, 134.

³ Arnold: "Steel Works Analysis," p. 195.

⁴ Waterhouse: *Chem. News*, 88, 198.

consequence ensued. With 2 per cent. hydrochloric acid, the hard mass softened and loosened from the bottom of the beaker after a short digestion; it was filtered off, washed, and the titanium dioxide in the filtrate estimated.

	Weight of solution. Grams.	TiO ₂ taken. Gram.	TiO ₂ in filtrate. Gram.
(19).....	11.181	0.1052	0.0020
(20).....	11.158	0.1051	0.0025

The residue containing the phosphotitanate still retained a large quantity of basic ferric salts, and, on following out the method of analysis as given, the final precipitation of the titanium dioxide had to be made in the presence of a considerable quantity of iron reduced to ferrous condition by sulphur dioxide. It is well known that unless the amount of iron be small, the separation under these circumstances is incomplete and in this experiment both of the precipitates of titanium dioxide were markedly contaminated with ferric oxide. To acquire further information, the experiment was repeated with slight modifications. The same quantities of titanium dioxide and ferric sulphate were taken; the baking lasted six hours; the mass was then digested with 50 cc. of 2 per cent. hydrochloric acid for two hours and finally boiled for half an hour. After filtering, estimations of the iron and titanium in the filtrate were made; the insoluble residue was returned to the beaker, 50 cc. of 4 per cent. hydrochloric acid added, and digestion carried on for fifteen hours at a temperature of 60° C. The solution was again filtered and the iron and titanium estimated in the filtrate.

	TiO ₂ extracted.	Total TiO ₂ extracted.	Fe extracted.	Total Fe extracted.
Two per cent. HCl (21).....	0.0048	0.1700
(22).....	0.0022	0.1140
Four per cent. HCl (21).....	0.0040	0.0088	0.1373	0.3073
(22).....	0.0037	0.0059	0.1151	0.2291

Taken: TiO₂ = 0.1050 gram. Fe = 0.5000 gram.

Taking mean values, 2 per cent. hydrochloric acid extracted 28 per cent. of the iron present and 3.5 per cent. of the titanium dioxide; 4 per cent. hydrochloric acid extracted 54.6 per cent. of the iron and 7 per cent. of the titanium dioxide.

A third trial was made with a titaniferous magnetite containing 44 per cent. of iron and 13 per cent. of the titanium dioxide. To 1 gram of the ore in impalpable powder were added

1 gram ammonium phosphate and 20 cc. of concentrated hydrochloric acid, and digestion at a temperature of nearly 100° C. was carried on for seven hours. The solution was evaporated to dryness, baked for five hours, digested with 2 per cent. hydrochloric acid for half a day and finally boiled for a short time. The same process was repeated with portions of the same acid of greater strength.

	TiO ₂ extracted.	Total TiO ₂ extracted.	Fe extracted.	Total Fe extracted.
Two per cent. HCl	{ (23)... 0.0043	0.2069
	{ (24)... 0.0054	0.2175
Four per cent. HCl	{ (23)... 0.0036	0.0070	0.1510	0.3579
	{ (24)... 0.0048	0.0102	0.1288	0.3463
Six per cent. HCl	{ (23)... 0.0085	0.0164	0.0483	0.4062
	{ (24)... 0.0080	0.0182	0.0506	0.3969

Quantities present in sample: TiO₂ = 0.130 gram; Fe = 0.440 gram.

Taking mean values we get:

	2 per cent. HCl. Per cent.	4 per cent. HCl. Per cent.	6 per cent. HCl. Per cent.
TiO ₂ extracted.....	4	7	13
Fe extracted.....	48	80	91

The serious inaccuracies to which the process is subject nullify its value as a method of separation, and only the possibility of its employment as a rapid, approximate method for technical work remains.

For such a purpose the following points should be noted. The baking should be thorough but not necessarily long; probably an hour at about 200° C. is sufficient. Four per cent. hydrochloric acid should be used for the extraction of the iron, boiling until solvent action apparently ceases; if there remain a considerable quantity of reddish ferric salts, the strength of the hydrochloric acid may be raised to 6 per cent., which should on boiling almost complete the extraction. If 4 per cent. acid has been used, the probable loss in the titanium dioxide will be from 5 to 10 per cent., with 6 per cent. hydrochloric acid, from 10 to 15 per cent.

HILGER AND HAAS' METHOD.

While studying the separation of titanium and tin, Hilger and Haas¹ discovered that by igniting the mixed oxides in hydrogen and then boiling with dilute sulphuric or hydrochloric acid, the reduced tin could be dissolved without apparent loss in titanium. The method was also applied to the separation of titanium and

¹ Hilger and Haas: *Ber. d. chem. Ges.*, 23, 458.

iron, but no analytical results could be found in any of the literature to which the writer had access. For the analysis of ores and minerals the following process is recommended by the authors. The finely ground material is treated with sulphuric and hydrofluoric acids; after the removal of the silica, the latter acid is expelled by evaporation and the solution is transferred to a casserole, neutralized with potassium hydroxide, 2 grams sulphuric acid added, and the volume made up to 400 cc. The liquid is then boiled for six hours, the bulk being kept constant by adding water and the precipitated titanium dioxide filtered off; the acidity of the filtrate is again adjusted to 0.5 gram sulphuric acid per 100 cc., and a further boiling is carried on to recover any titanium which may still remain in solution. The total precipitate, which contains all the tin and a small quantity of iron, is then reduced in hydrogen for from fifteen to thirty minutes and boiled gently with 20 per cent. hydrochloric acid for half an hour. Tin and iron are dissolved, the titanium dioxide is filtered off, and, unless the amounts are small, the reduction and extraction are repeated.

Ledebur¹ has described a modification of the process suitable for iron ores. The ore is reduced in hydrogen, boiled with dilute sulphuric acid 1 : 40, and the insoluble residue filtered off, treated with hydrofluoric acid, dried, fused with sodium carbonate, leached, re-fused with potassium bisulphate and the melt dissolved in water. The titanium dioxide is then precipitated by boiling for an hour at a bulk of 450 cc.; no precautions for regulating the acidity of the solution are stated.

The important point is evidently the insolubility of the titanium dioxide, either as it occurs naturally or in the form of metatitanic acid; some experiments covering this question were, therefore, made. For convenience, an iron ore was first tested according to Ledebur's directions, as given above. One gram of a titaniferous magnetic was reduced at a red heat in hydrogen for an hour and boiled in dilute sulphuric acid, 1 : 40, for twenty minutes, the evolution of hydrogen ceasing after about ten minutes. Estimations were then made in the filtrate by color. In one experiment there was found 5 milligrams titanium dioxide, in another 5.2 milligrams. These would cause losses of 4 per cent. in the titanium dioxide found.

¹ Ledebur: *Leitfaden f. Eisen. Lab.*, 5th edition, p. 38.

already been discussed were chosen because of the economy of time which they appeared to offer; of the other processes or modifications recently proposed which have come under the writer's notice, none appear to be free from objection, either on account of inaccuracy or of the amount of time required for their operation.

When in search of rapid methods one turns first to volumetric analysis, but unfortunately in that direction no accurate process for the estimation of titanium is available. Wiegand¹ has studied the volumetric method proposed by Pisani² and, with all the improvements which could be devised, found it still unsatisfactory. In the presence of titanium and iron the solution was reduced with zinc until the color no longer changed, then potassium permanganate was slowly added till a drop gave a red coloration with potassium thiocyanate. Errors of 3 to 4 per cent. are numerous among the results given; even with portions of a pure solution of titanium sulphate which were reduced and reoxidized, the errors in determination averaged 3.7 per cent. Wells and Mitchell,³ investigating the same method, proceeded upon a slightly different plan. Two equal quantities of a solution containing iron and titanium were taken, one was reduced with hydrogen sulphide, the other with zinc, the titanium being estimated by difference. Even with elaborate precautions, no better results were obtained. In ten determinations published, the lowest error was 2 per cent. and the highest 6 per cent.

Walker⁴ has founded a method of separation from iron upon the observation that salts of titanium oxidized with hydrogen peroxide are not immediately precipitated by ammonia. An excess of the former reagent is added to the solution containing the two elements as sulphates and the whole is allowed to flow gently into ammoniacal hydrogen peroxide. Three separations were found to be necessary to separate 0.1 gram iron from the same amount of titanium dioxide; the results are excellent, but the number of operations appear to be a drawback.

In Rothe's⁵ method, which has found such extended use for the separation of nickel and iron, titanium, if present, remains

¹ Wiegand: *Ztschr. anal. Chem.*, 21, 510.

² Pisani: *Compt. Rend.*, 89, 289.

³ Wells and Mitchell: *This Journal*, 17, 878.

⁴ Walker: *This Journal*, 20, 513.

⁵ Rothe: *Mitth. König. Tech. Vers. Anst.*, Berlin, 1892, Part III.

in the acid solution and is therefore separated from iron; no analytical data are available, however, for guidance in forming an opinion.

Mathews¹ has described as a means of separating iron from titanium, zirconium, and some of the rare earths, a modification of Rothe's method. The mixed, dried chlorides of the elements are heated with absolute ether and dry hydrochloric acid gas; the ferric chloride dissolves, leaving as a residue the chlorides of the other element or elements.

Although not at present very promising from the standpoint of speed, the three methods last described have interesting possibilities and deserve investigation; unfortunately, the time for a study of their efficiency has hitherto been lacking, but it is hoped that some experiments in this direction will shortly be carried out.

As a result of the study which has been made, it has been found that Baskerville's method is superior in accuracy to either of the others, but the writer is of the opinion that the modification of Gooch's method, described by Blair, is the best which has yet been made public. An excellent and detailed description of this process is given by Pope;² it does not take more time to carry out than does Baskerville's, and in the hands of the writer, has proved the more accurate.

FACULTY OF APPLIED SCIENCE,
UNIVERSITY OF TORONTO, July, 1903.

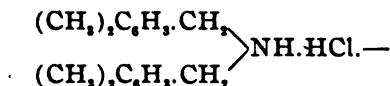
[CONTRIBUTION FROM THE LABORATORY OF THE UNIVERSITY OF MINNESOTA.]

REDUCTION OF 2,5-DIMETHYLBENZALDAZINE AND THE PREPARATION OF SOME OF ITS SALTS.

BY EVERHART PERCY HARDING AND LILLIAN COHEN.

Received July 25, 1903.

*Preparation of the Hydrochloride of 2,5-Dimethyldibenzylamine.*³



—From 2 to 5 grams of 2,5-dimethylbenzalazine, prepared

¹ Mathews: This Journal, 20, 846.

² Pope; *Trans. Am. Inst. Min. Eng.*, 20, 372.

³ The free base—dimethyldibenzylamine has not yet been analyzed.

according to the method of Curtius and Jay¹ from 2,5-dimethylbenzaldehyde, prepared by the Gatterman-Koch method,² were dissolved in 95 per cent. alcohol, some glacial acetic acid, and an excess of zinc dust added, and the flask with reflux condenser placed upon a water-bath, and the mixture gently boiled for about four hours. Upon the addition of very dilute sulphuric acid the unchanged azine was filtered off and to the filtrate, made strongly alkaline with sodium hydroxide, was added dilute hydrochloric acid. Upon standing some time, the hydrochloride crystallized out in the form of white, satin-like needles which crystallized from dilute alcohol in the form of colorless, prismatic needles and which melted at 227°. An analysis showed the following percentage composition:

	Calculated. Per cent.	Found. Per cent.
Carbon	74.74	74.70
Hydrogen	8.30	8.48
Nitrogen	4.84	4.91
Chlorine	12.11	12.10

2,5-Dimethyldibenzylaminehydrochloride is very soluble in ethyl and methyl alcohols and benzene, and slightly soluble in acetone. It is insoluble in cold but soluble in hot water.

2,5-Dimethyldibenzylamine Nitrate, $C_{15}H_{22}N.HNO_3$.—The nitrate was prepared by adding sodium hydroxide to a water solution of the hydrochloride and then treating the solution with dilute nitric acid. The nitrate precipitated at once as a white, crystalline substance which recrystallized out of dilute alcohol in the form of thin, colorless plates of the monoclinic system which melted at 215°. The analysis gave 8.86 per cent. N. Calculated, 8.80 per cent.

The nitrate is soluble in ethyl and methyl alcohols and insoluble in benzene. It is very difficultly soluble in acetone. It is soluble in hot, but insoluble in cold water.

2,5-Dimethyldibenzylamine Picrate, $C_{15}H_{23}N.C_6H_2(NO_2)_3OH$.—The picric acid derivative was prepared by adding to a concentrated alcoholic solution of the free base a concentrated alcoholic solution of the calculated amount of picric acid. The picrate was then precipitated by adding water. The voluminous precipitate was then filtered off, washed well with water and crystallized out of dilute alcohol. Upon crystallizing several times out of alcohol, the short sulphur-yellow prisms melted at 142°.

¹ *J. prakt. Chem.*, Neue Folge, 89, 43.

² *Ber. d. chem. Ges.*, 30, 1622.

The picrate is soluble in ethyl and methyl alcohols and very soluble in benzene and acetone. It is slightly soluble in hot but insoluble in cold water.

2,5-Dimethyldibenzylamine Mercuric Chloride,

$(C_{12}H_{23}N.HCl)_2.HgCl_2$.—A concentrated water solution of mercuric chloride was added to a concentrated water solution of the hydrochloride. Upon standing, a white precipitate crystallized out which, upon recrystallizing out of alcohol, crystallized in long, colorless prisms which melted at 157.5° . The crystals are very soluble in ethyl and methyl alcohols and less soluble in benzene. They are very soluble in warm and slightly soluble in cold water.

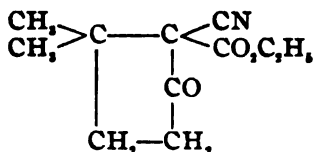
2,5-Dimethyldibenzylamine Chlorplatinate,

$(C_{12}H_{23}HCl)_2.PtCl_4$.—The platinum double salt was prepared by adding to a concentrated water solution of the hydrochloride a concentrated solution of chlorplatinic acid. The salt soon precipitated which recrystallized from alcohol in the form of reddish yellow, prismatic needles which melted at 188° . An analysis gave 21.22 per cent. of platinum, calculated 21.01 per cent. The double salt is soluble in ethyl and methyl alcohols and in acetone. It is insoluble in benzene and in hot and cold water.

SYNTHESIS OF β -METHYLADIPIC ACID.¹

BY WILLIAM A. NOYES AND IRVING J. COX.

SOME time ago² one of us found that dimethylcyanocarboxethylcyclopentanone,



is decomposed by sodium hydroxide with formation of the sodium salts of malonic and hydroxyisocaproic acids. So far as we are aware, no other similar elimination of a carbon atom, by saponification, from a cyclic compound has been observed, and it seemed of interest to determine whether the reaction is a general one. To throw further light on this question, we have attempted to

¹ The work here described formed the basis of a thesis for the degree of Bachelor of Science at the Rose Polytechnic Institute.

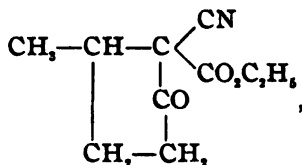
² This Journal, 23, 396.

prepare a similar compound containing one methyl group instead of the two. The amount of the desired compound formed was too small for our original purpose, but some new compounds which seem worthy of a brief description were obtained.

Reduction of Levulinic Acid.—The levulinic acid was prepared from sugar and was purified by one distillation under diminished pressure.¹ From 75 to 80 grams of the acid were obtained from 500 grams of sugar.

For reduction, the acid was divided into portions of 10 grams each, and each portion dissolved in 25 cc. of water. About 225 grams of 3 per cent. sodium amalgam were added slowly to each portion, excessive heating being avoided. After standing for thirty-six hours, the different portions were united, acidified with sulphuric acid, 1 : 1 by volume, and the valerolactone distilled in a current of steam. The distillate was boiled with enough sodium hydroxide to make it alkaline and the solution evaporated nearly to dryness. The residue was acidified, the solution extracted with ether, and, after drying with sodium sulphate and distilling off the ether, the lactone was distilled under atmospheric pressure. Fifty-one grams of the lactone were obtained from 81 grams of the acid. The method is similar to that of Neugebauer,² but differs in detail and, especially, in that Neugebauer took fourteen days for the reduction. Our yield was also a little better.

Condensation of γ -Chlorvaleric Ester and of γ -Bromvaleric Ester with Cyanacetic Ester.— γ -Chlorvaleric ester was prepared by treating the lactone with absolute alcohol and hydrochloric acid. By condensing the chlorester with cyanacetic ester by means of sodium ethylate³ and distilling the resulting products under diminished pressure, a small amount of a crystalline product, which melted at 185°, was obtained from the portion which came over last. It is believed that this compound was 2-methyl-1,1-cyancarboxethylcyclopentanone,



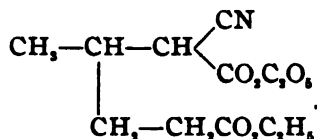
¹ Noyes' "Organic Chemistry for the Laboratory," p. 67.

² *Ann. Chem.* (Liebig), 227, 100.

³ *This Journal*, 23, 397.

but the amount obtained was too small for analysis or for further examination.

β -Methyl- α -cyanadipic Ester,

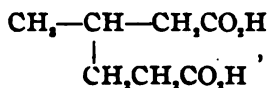


—When γ -bromvaleric ester is condensed with cyanacetic ester, methylcyanadipic ester was formed instead of the cyclic compound, which was desired. This boils at 175° - 185° under a pressure of 20 mm. The yield was much greater than with the chloresther. The analysis gave: C, 60.29, 60.09; H, 7.97, 7.99; N, 5.96. Calculated for C, 59.75; H, 7.83; N, 5.81.

3-Methylhexanoic-1,2',6- Acid.—By saponifying with alcoholic sodium hydroxide, evaporating, dissolving in water, acidifying and extracting with ether, the corresponding tribasic acid was obtained. On slow evaporation of its aqueous solution, the acid crystallizes in plates which melt and decompose at 127° - 128° .

The Calcium Salt, $(\text{C}_8\text{H}_9\text{O}_6)_2\text{Ca} + 3\text{H}_2\text{O}$, is sparingly soluble in water. The analysis gave: Ca, 20.92, 20.63; H_2O at 200° , 9.20, 9.36. Calculated for Ca, 20.83; H_2O , 9.37.

β -Methyl Adipic Acid,



if formed when the tribasic acid is heated for a short time to 200° . After crystallization from benzene, the acid melted at 89.2° . On titration with lime-water, 0.0632 gram required the equivalent of 7.73 cc. N/10 alkali. Theory requires 7.90 cc. In a second experiment, 0.0315 took 3.86 cc.; calculated, 3.94 cc.

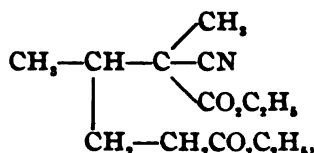
The melting-point of *active* β -methyladipic acid is given by Manasse and Rupe¹ as 88.5° - 89° ; by Baeyer² as 89° ; by Semmler³ as 84.5° ; and by Wagner⁴ as 93° - 94.5° .

¹ Ber. d. chem. Ges., 27, 1820.

² Ibid., 29, 30.

³ Ibid., 28, 3516.

⁴ Ibid., 27, 1642.

2,3-Dimethyl-2-cyanadipic Ester,

was prepared, as usual, by condensing the monomethyl ester with methyl iodide by means of sodium ethylate in an alcoholic solution. It boils at 181° - 194° under a pressure of 29 mm.

The analysis gave:

Calculated for $\text{C}_{13}\text{H}_{21}\text{O}_4\text{N}$, C, 61.18; H, 8.24; N, 5.49. Found: C, 61.12, 61.95; H, 8.49, 8.53; N, 5.43.

2,3-Dimethyl-1,2',6 Acid.—The ester was saponified with much greater difficulty than the corresponding monomethyl ester. It required two days' heating on the water-bath with sodium hydroxide before the evolution of ammonia was complete. The resulting tribasic acid crystallizes in pearly white granules which melt at 159° . On titration with lime-water, 0.0361 gram took the equivalent of 5.07 cc. N/10 alkali, and 0.0407 gram took 5.55 cc.; calculated, 4.97 cc. and 5.60 cc.

α,β -Dimethyladipic Acid.—The dimethyladipic acid, formed by heating the tribasic acid to 200° , could not be induced to crystallize. An analysis of its silver salt gave 55.45 per cent. silver; calculated for $\text{C}_8\text{H}_{12}\text{O}_4\text{Ag}_2$, 55.67 per cent.

The copper salt from another preparation gave only 24.90 and 24.98 per cent. copper instead of 27.00 per cent. calculated. A salt containing 1 molecule of water would give 24.68 per cent. of copper, and it seems probable that this was the composition of the salt, but such evidence is not altogether satisfactory. We had no time for the further investigation of the salt.

NOTES.

Note on the Avery-Beans Method for the Determination of Arsenious Acid in Paris Green.—This method rests on the principle that arsenious acid may be titrated with iodine in the presence of cupric salts, provided an alkaline tartrate be present. As originally published,¹ the method gives accurate results only when

¹ This Journal, 23, 485.

no free, white arsenic appears on treating the green with cold dilute hydrochloric acid. In this laboratory I have, for some time, treated such greens as show a tendency to separate out white arsenic as follows: The sample is treated with hydrochloric acid (approximately 0.5 N) solution and boiled gently. Five to 10 cc. of acid for each 0.1 gram of green is sufficient. No loss of arsenic by volatilization takes place unless the solution becomes concentrated to less than one-half its original volume. If solution is not effected, add a cold saturated solution of sodium acetate, using about 3 grams of the salt for each 0.1 gram of the green originally weighed out, and boil till all arsenious acid dissolves. The dilute acid dissolves all copper and what we may call "firmly combined white arsenic." The concentrated acetate solution dissolves all white arsenic left by the acid. The proportions of the two solvents may be varied to meet the requirements of individual greens, but all copper should be in solution before the acetate is added. After solution is effected, an alkaline tartrate and solid bicarbonate are added and the diluted solution titrated as usual.

LINCOLN, NEB., Sept. 1, 1903.

S. AVERY.

NEW BOOKS.

ANALYTICAL CHEMISTRY. Vol. I. QUALITATIVE ANALYSIS. By F. P. TREADWELL, PH.D., Professor of Analytical Chemistry in the Polytechnic of Zurich. Translated from the second German edition by WILLIAM T. HALL, S.B., Instructor in Chemistry, Massachusetts Institute of Technology. New York: John Wiley and Sons. 1903. Price, \$3.00.

This book is an amplified reproduction of the lectures on qualitative analysis that Professor Treadwell has delivered yearly at Zurich since 1882. The first German edition was issued in 1899 and met with such a favorable reception that it was followed two years later by a second edition which now appears in English form.

The general plan is that usually followed in text-books on this subject. Under the heading General Principles, an introduction of some thirty pages treats briefly of precipitation, oxidation and reduction, hydrolysis, mass action and the ion theory. The last two subjects are alluded to occasionally in the body of the text but are not made the basis of the method of presentation.

The chief feature of the work is the treatment of the action of the various reagents on solutions of pure salts. Explanations of the mechanism of these reactions are introduced in detail, in connection with which free use is made of equations and graphical formulas. The result is a valuable work for ready reference, especially valuable in that it embodies the ideas of a chemist of twenty years' experience in teaching the subject.

The book is an expansion of the old style text-book on the subject and its chief faults are inherent in the method of presentation. It is to be regretted that, with the exception of the pages in the introduction giving directions for the determination of the sensitiveness of reactions, there is scarcely a hint in the whole book that the majority of reactions cannot be represented quantitatively by an equation unless the conditions as to the temperature, concentration, etc., are allowed to vary only within relatively narrow limits. An occasional lack of conservatism of statement about reactions which are complicated and uncertain, or vary under slightly varying conditions, is also unfortunate. The impression is conveyed that such reactions have actually been proved to take place in the way explained and often a distinction is not drawn sharply enough between what is known to happen and what is supposed to happen. For example we find such statements as the following: "The oxidizing action of nitric acid depends upon the formation of the anhydride which then breaks down into nitric oxide and oxygen," page 4; "if an excess of hydrogen peroxide is used" in oxidizing chromic acid to chromium peroxide "a lively evolution of oxygen will ensue; the chromium peroxide as well as the hydrogen peroxide will be reduced. The oxygen comes from the hydrogen peroxide while the hydrogen of the latter is oxidized by the chromium peroxide to water," page 85.

These faults are especially noticeable in the supplement which treats of the rarer metals. Much of the matter here given has no place in a book of this sort. The reactions of the "pure" salts of these elements are of interest, if it is actually known what these reactions are; but a treatise on Qualitative Analysis which gives the impression to the student that the behavior of the rare elements is as definitely and exactly known as that of iron, and which, aside from a table giving a method of analysis for gadolinite, ignores the separation of these elements from the commoner ones, might better leave the whole field of the rarer elements untouched. We

note that "there are no characteristic dry reactions" of Thorium, page 16. Of the nine wet reactions enumerated, not one is characteristic. The only characteristic reaction of the element, that with a solution of potassium trinitride¹ containing hydronitric acid, is not mentioned. Under neodymium and praseodymium we find the statement "it is very difficult to separate these two metals from one another. It is accomplished only by repeated fractional crystallization of the ammonium double nitrate." The fact that the presence of another base, such as lanthanum, makes this separation possible in comparatively few crystallizations is not mentioned.

The proof-reading leaves something to be desired; but in a book that contains as many formulas and equations as this, an occasional error is almost unavoidable. That a few typographical errors in the first German edition should have survived not only the second edition in that tongue but a translation as well, is, however, surprising. Such errors appear in equations on pages 157 and 206. Of other errors may be cited the precipitation of cobalt by potassium nitrate, page 143, and the use of nitric for hydrochloric acid on page 235, line 9. In general, the methods used in the separation and detection of the elements have been well chosen. Hillebrand's method for the detection of the vanadium is introduced in this edition. The only seriously faulty method which strikes the eye is that for the detection of hydrochloric acid in the presence of hydrobromic and hydriodic acids. This is attempted by fractional precipitation of the silver salts until finally a white precipitate is produced. The adoption of a test of this sort is inexcusable when we have at our command the excellent separations based on the oxidation of hydrobromic and hydriodic acids by appropriate oxidizing agents.²

The plate of the spectra is very poor, but the typography and press work of the book are good, and the translation has been well done.

THEODORE WHITTLESEY.

RADIUM AND OTHER RADIO-ACTIVE SUBSTANCES, ETC. BY WILLIAM J. HAMMER, Consulting Electrical Engineer. New York: D. Van Nostrand Company. Price, \$1.00.

This booklet of 72 pages represents a lecture delivered before a joint meeting of the American Institute of Electrical Engineers

¹ L. M. Dennis: *This Journal*, 18, 947.

² See Hart: *Am. Chem. J.*, 6, 346; Benedict and Snell: *This Journal*, 28, 809.

and the American Electrochemical Society. The section devoted to radium and radio-active bodies is very instructive and exceedingly entertaining. In the letter to the author, M. Curie writes, "Where is the source of this energy? Both Mme. Curie and myself are not able to go beyond hypotheses. One of these consists in supposing the atoms of radium evolving and transforming into another simple body and, despite the extreme slowness of that transformation, which cannot be located during a year, the amount of energy involved in that transformation is tremendous."

Every chemist will find in the various paragraphs in this book much material for reflection. Having studied the data here submitted and read Barker's most interesting fasciculus entitled "Radio-activity and Chemistry," he will have had brought to him a very complete and accurate account of the marvelous results which have been noticed in recent years, along lines which he probably never dreamed could include his beloved and simple atom. It is said the lamented Rowland once remarked, "that a Steinway grand piano was a comparatively simple piece of mechanism compared with an iron atom." It would indeed seem after perusing the pages of Mr. Hammer's book, as if not only the iron atom, but the atoms of many more of our elements were not only complex, but were undergoing a subtle and constant change.

The second section of Mr. Hammer's book gives in a very succinct form most interesting accounts of the properties and application of selenium, while in the third section there is presented briefly, it is true, but at the same time most interestingly, an account of the treatment of diseases by ultra-violet rays. It is here that a description of the Finsen Institute at Copenhagen is given with a description of the treatment of *Lupus vulgaris*.

This publication deserves to be widely read because of the new facts which it presents and because of its suggestiveness. Certain typographical errors appear, but these will no doubt be corrected in a subsequent edition of the book. EDGAR F. SMITH.

DIE CONSTITUTION DES KAMPHERS UND SEINER WICHTIGSTEN DERIVATE,
VON OSSIAN ASCHAN. Braunschweig: Friedrich Vieweg und Sohn.
1903. pp. xi + 117.

So many workers have busied themselves with the subject of camphor, and the material accumulated has become so com-

plicated, that such a book as the present one is very welcome. Without attempting to give any details as to physical properties or methods of preparation for the derivatives of camphor, it does give a very clear oversight of nearly all of the relationships among those compounds which are important in establishing its structure. The work includes: 1, A brief statement with regard to each of the thirty-three formulas which have been proposed for camphor (or for camphoric acid); 2, a summary of the facts which must be considered in deciding what is the true structure; 3, a criticism of the formulas which have been proposed. This criticism demonstrates, conclusively, that of all the formulas proposed Bredt's is the only one which can now be considered as possible; 4, a consideration of other important decomposition products of the camphor; 5, a discussion of the structure of camphene and borylene.

When we consider the very large number of compounds which must be spoken of in such a discussion and the confusion which exists in the nomenclature of some of these bodies, it would seem almost impossible to avoid some mistakes. Very few have been noticed. The most important are the following: On page 61, α -dihydrohydroxy- β -campholytic acid is spoken of as identical with $[\gamma]$ -dihydrohydroxy- α -campholytic acid; on page 57, Walker's "allocampholytic acid" is called " α -campholytic acid"; and on page 68, the active α -campholytic acid is not properly distinguished from the racemic form of the same compound.

The student who is interested in the special study of camphor will find the book a most useful summary of our present knowledge of the subject, and the general student can scarcely find a better illustration of the nature of the work which must be done for the determination of the structure of a complex organic compound. And the fact that the solution of the problem which has been reached has the support of every one familiar with this particular field, in spite of the diversity of opinion which has prevailed till very recently, demonstrates that very positive results have finally been obtained.

W. A. NOYES.

L'ACÉTYLÈNE. THÉORIE. APPLICATIONS. BY MARIE-AUGUSTE MOREL.
Paris: Libraire Gauthier-Villars. 1903. 8 vo. xii + 169 pp.

This book is written by an engineer and gives a thermochemical and mathematical treatment of its subject. Its contents are well

indicated by the chapter headings: I, General remarks upon the constitution of the hydrocarbons; II, general remarks upon the metallic carbides and the generation of the hydrocarbons; III, calcium carbide, its physical and chemical properties, its applications; IV, acetylene, its preparation, its physical, chemical, and toxic properties; V, the calorific, optical, and explosive properties of acetylene. Burners: VI, The different applications of acetylene. Lighting, heating, motive force: VII, New considerations upon generating apparatus for acetylene gas. A note upon the thermodynamic potential is appended. The sixth chapter begins with a brief history of artificial illumination in general.

There are a few noticeable errors. On page 33 an equation is balanced, using the formula CaCl for calcium chloride. On pages 40 and 54 no attention has been paid to the work of Keiser,¹ who has shown that cuprous acetylide contains no oxygen and no hydrogen. The author gives it the formula $\text{C}_2\text{HCu}_2\text{OH}$ on page 40. Dr. Auer von Welsbach's name is spelled "Velbasch" on page 101. On page 150, a figure is given to parts of which reference is made in the text by letters, none of which appear in the figure. Some of these may be the fault of the printer.

The book is very well written, although the author occasionally lapses into poetical expressions. He is, perhaps, ultra-enthusiastic in favor of the use of acetylene for lighting anything or any place, but all his comparisons are made fairly and do not deal in generalities.

Very little apparatus is described, but the author says in his preface that he intends to describe only that which is most nearly correct theoretically.

The typographical work is generally good.

The book is of value to engineers and others who are interested in the installation of apparatus for the production of acetylene. It is also a useful addition to the library, for it gives a condensed and systematic form, quite a complete résumé of the chemistry and uses of acetylene.

BENTON DALES.

¹ *Am. Chem. J.*, 14, 285.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN.]

AN EXPERIMENT UPON THE INFLUENCE OF THE FINE- NESS OF GRINDING UPON THE CLINKERING OF PORTLAND CEMENT.

BY E. D. CAMPBELL AND S. BALL.

Received September 11, 1903.

IN A paper entitled "Some Preliminary Experiments upon the Clinkering of Portland Cement,"¹ one of the authors has reported some results obtained in a laboratory rotary cement kiln. The calcium carbonate used in all the preliminary experiments was in the form of a very light marl, so that when clinkering took place it was accompanied by very marked contraction in volume. It was suggested that a burning on raw material, such as is used in the cement mills of Eastern Pennsylvania, might give somewhat different results from those obtained from the light marl mixed with clay, and so it was decided to make a couple of experiments with rock-cement mixtures. The material employed in the two experiments, to be later described, was a ground raw mixture just as it is fed into the rotary for the dry process. This raw mixture is that used by one of the best Lehigh Valley mills and was furnished for these experiments through the courtesy of the management.

¹ This Journal, 24, 969.

Before detailing the experiments made upon the cement-rock mixture, we wish to describe the method now employed in this laboratory for determining the actual temperature attained by the pieces of clinker in passing through the rotary. In the first papers published by one of us on "A Rotary Cement Kiln for use in the Laboratory,"¹ the method of measuring the temperature of the furnace is described. In this method, the temperature attained by a Le Chatelier thermocouple, insulated with porcelain tubing and protected with sheet platinum, is observed. But this temperature was supposed to be 35° to 40° C. lower than that attained by the clinker. The temperatures given in the paper, first quoted in this article as representing the temperatures attained by the clinker, are based on the assumption that the clinker becomes 35° hotter than the protected thermocouple. It is true that if the bare couple be placed in the rotary, it will reach a higher temperature than that shown by the protected couple. This does not, however, warrant the assumption that pieces of clinker in contact with the rotary lining will attain as high a temperature as the bare couple. It was because of the feeling that the relation between the temperature of the clinker and that of the fixed couple was not what we have assumed in our previous work, that a series of experiments was made to determine the relation of these temperatures. A calibration of the fixed thermocouple was made, as in our previous work, by careful comparison of the electromotive force with that of a couple standardized by the physikalische-technische Reichsanstalt. The electromotive force at the melting-point of strictly pure platinum was also determined, and used in the calibration. Although an entirely new set of thermocouples and galvanometer were used in the present experiments, the temperatures recorded for the fixed thermocouple agreed within the limits of experimental error with those of our previous work. In order to determine the relation between the temperature attained by pieces of clinker and that observed at the fixed thermocouple, the following method was used: About 2 kg. of magnesite brick were crushed, and, after mixing with one-ninth its weight of a rather fusible clay, was ground to a fine powder. This mixture was moistened with enough water to enable it to be rolled out and cut into cubes, of about three-eighths inch, which were then dried. These cubes were passed through

¹ This Journal, 24, 248.

the rotary at a full heat, the result being hard, well-sintered, but infusible "magnesite clinkers." A Seger cone of the standard size was placed in an assay muffle, the temperature of which was then raised until the top of the cone bent over enough to touch the bottom—the method usually employed for standardizing these cones. The extent to which this cone had rounded at the corners, etc., gave a standard with which to compare pieces of cone which had passed through the rotary. In testing the temperatures attained by the clinker in the rotary, a cone of low fusing-point ($990^{\circ}\text{C}.$) was first employed. Cones of this softening-point were broken into pieces of as nearly as possible the same size as the "magnesite clinker." When the rotary was filled with the magnesite, a piece of the cone was fed with the magnesite every four or five minutes. The temperature was gradually raised until the pieces coming out showed an extent of softening or fritting equal to that of the standard cone. This point was usually quite sharply defined, as when the pieces of cone attained this condition they would begin to stick either to each other or to adjacent pieces of magnesite. In this way our experiments were made with a number of cones of a higher softening-point, up to between 1500° and $1600^{\circ}\text{C}.$ These experiments showed that at the lower temperature the clinker does not get as hot as the fixed couple, but that it approaches the temperature of the fixed couple as the heat is raised, until at about $1270^{\circ}\text{C}.$ they are equal. At temperatures above $1270^{\circ}\text{C}.$, the clinker is hotter than the thermocouple, this difference amounting to very nearly 19° at $1600^{\circ}\text{C}.$ The relation of the "clinker temperature" to that observed at the fixed couple is shown in the following table:

TABLE I.

Observed temperature. $^{\circ}\text{C}.$	Clinker temperature. $^{\circ}\text{C}.$	Difference.
1000	984	-16
1100	1090	-10
1200	1196	-4
1300	1302	+2
1400	1407	+7
1500	1513	+13
1600	1619	+19

The "clinker temperatures," reported in experiments 104-105 to be described, were determined according to this table. The "clinker temperature," in our previously reported work, can be

easily derived by first subtracting 35° , thus obtaining the "observed temperature," and then applying the necessary correction according to the above table.

EXPERIMENT 104.




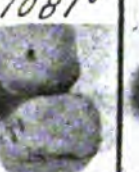









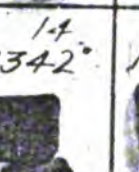
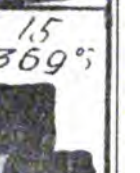


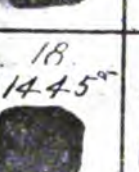

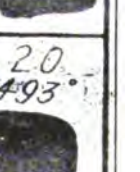
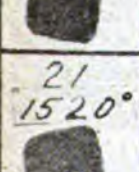
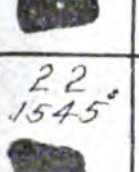
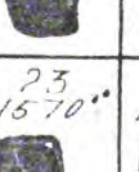
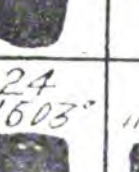
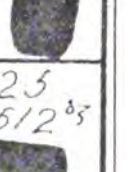
The material used in this experiment was, as mentioned earlier in this paper, the ground raw mixture just as it is fed into the rotaries of one of the leading Eastern cement-mills employing the dry process. The chemical composition of this mixture will be described under Experiment 105. A mechanical analysis of the raw mixture gave the following figures:

	Per cent.
Retained on 50-mesh sieve	3.1
" " 100 " "	11.3
" " 200 " "	13.2
Through 200-mesh sieve	72.4

This raw mixture was moistened with just enough water to allow it to be rolled out and cut into small cubes, as done in our previous work. The rotary furnace was fed with this prepared material, and samples of from 80 to 100 grams each were collected at twenty-five different temperatures ranging from 993° to 1612° C. When the desired amount of clinker had been collected at any given temperature, the temperature of the furnace was raised up to the next higher point desired, and the first 60 to 70 grams of clinker leaving the furnace rejected before the final sample was kept. The 60 to 70 grams of clinker, rejected between the sample saved, is the amount required to fill the furnace from the hot zone to the discharge end and, consequently, represents the clinker formed at heats intermediate between the desired temperatures. The change in appearance of the samples of clinker is shown in Plate I, made from a full-sized photograph.

Samples of these clinkers were ground with 1.5 per cent. calcium sulphate (dehydrated gypsum). The methods employed for determining the water required for normal consistency, the initial and final sets, and boiling tests were those employed in our previous experiments. The data obtained from Experiment 104 are summarized in the following table:

Ex 104 PLATE I

1 993° 	2 1028° 	3 1058° 	4 1081° 	5 1110° 
6 1134° 	7 1165° 	8 1187° 	9 1216° 	10 1247° 
11 1270° 	12 1295° 	13 1318° 	14 1342° 	15 1369° 
16 1393° 	17 1418° 	18 1445° 	19 1469° 	20 1493° 
21 1520° 	22 1545° 	23 1570° 	24 1603° 	25 1612° 

Temp. in degrees Cent.

TABLE II, EXPERIMENT 104.

Sample number.	Clinker temperature.	Water. Per cent.	Initial set.		Final set.		Boiling test.
			Hours.	Minutes.	Hours.	Minutes.	
1	993	39	..	24	3	53	Perfect pat.
2	1028	48	..	30	3	58	" "
3	1058	54	..	30	4	20	" "
4	1081	66	..	35	4	33	" "
5	1110	76	..	41	5	38	Badly cracked.
6	1134	75	..	48	6	5	Badly cracked, broken up, loose from glass.
7	1165	76	..	17	1	45	{ Cracked after twenty-four hours. Boiling test, badly cracked and broken up.
8	1187	60	..	1	..	16	Slightly cracked and warped, loose from glass, quite strong.
9	1216	55	..	½	..	19	Loose from glass, moderately strong.
10	1247	47	..	1	..	6	Badly cracked, disintegrated, very weak.
11	1270	43	..	1	..	4	Warped, cracked, almost completely disintegrated.
12	1295	38	..	2	..	4½	" " " "
13	1318	37	..	3	..	11	Completely disintegrated.
14	1342	32	..	7	1	38	" " " "
15	1369	31½	..	12	1	26	" " " "
16	1393	30½	..	23	4	8	Completely disintegrated, coarse-grained.
17	1418	28½	..	33	4	..	Almost completely disintegrated.
18	1445	26	..	21	3	48	" " " "
19	1469	26	..	33	3	50	Slightly warped, badly cracked, very weak.
20	1493	26½	..	13	2	53	Slightly warped, cracked, very weak.
21	1520	25½	..	34	4	9	Badly warped, cracked, very weak.
22	1545	25	1	..	5	..	Slightly warped, cracked, quite strong.
23	1570	24	..	50	4	6	" " " "
24	1603	23	..	32	3	50	{ Badly warped, cracked very weak. (This sample was ground too coarsely.)
25	1612	23½	..	17	3	48	Very slightly warped, cracked, very strong.

The appearance of the pats from Experiment 104 is shown in Plates II, III, IV and V.

EXPERIMENT 105.

The material used in this experiment was the same raw material as that used in Experiment 104. Before adding water and molding into cubes for burning, the dry mixture was ground in a pebble mill for five hours. The jar in which the grinding was done had a special lining made for this purpose of the best Berlin porcelain. The pebbles used were carefully selected, smooth flints. A mechanical analysis of the mixture after five hours' grinding gave the following results:

	Per cent.
Retained on 100-mesh sieve.....	0
" " 200 " " 	2
Through 200-mesh sieve.....	98

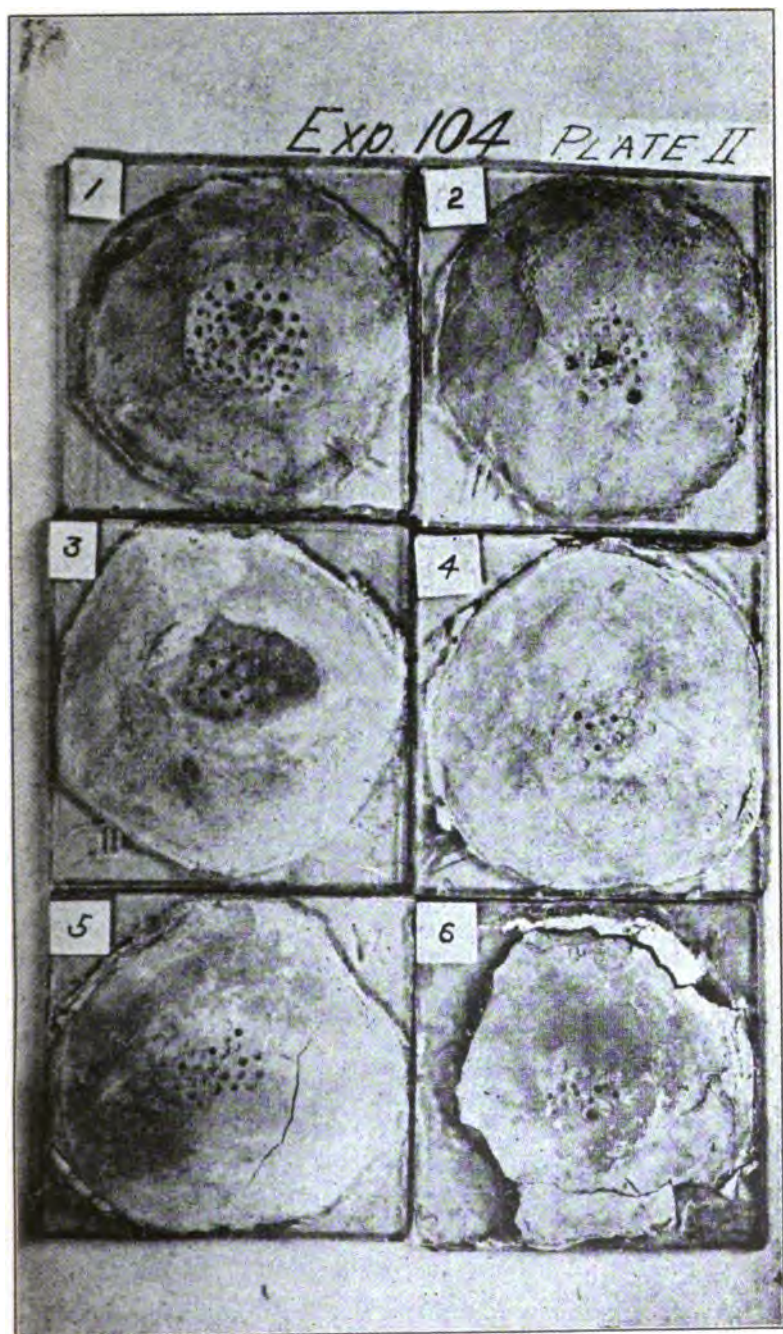
That material ground in this porcelain-lined jar mill does not take up sufficient impurities to seriously alter the composition was determined in two ways: First, 2 kilograms of crushed crystalline calcite were ground for three hours. The combined per cent. of silica, alumina, and ferric oxide before grinding was 0.71; after grinding three hours, the material showed 0.75 per cent. Second, the clinker from Experiment 104 gave total silica and undecomposed silicates, 22.02 per cent., while that from Experiment 105 gave 22.06 per cent.

The raw mixture used had the following composition: SiO_2 , 14.09; Al_2O_3 , 5.94; Fe_2O_3 , 1.67; CaO , 41.21; MgO , 1.76; SO_3 , 0.39; loss on ignition, 34.60. The finely ground, raw material was mixed as in the previous experiment with enough water to allow it to be rolled out and cut into cubes for burning. From this prepared material, twenty-four samples of the clinker were collected at temperatures ranging from 1022° to 1627° C.

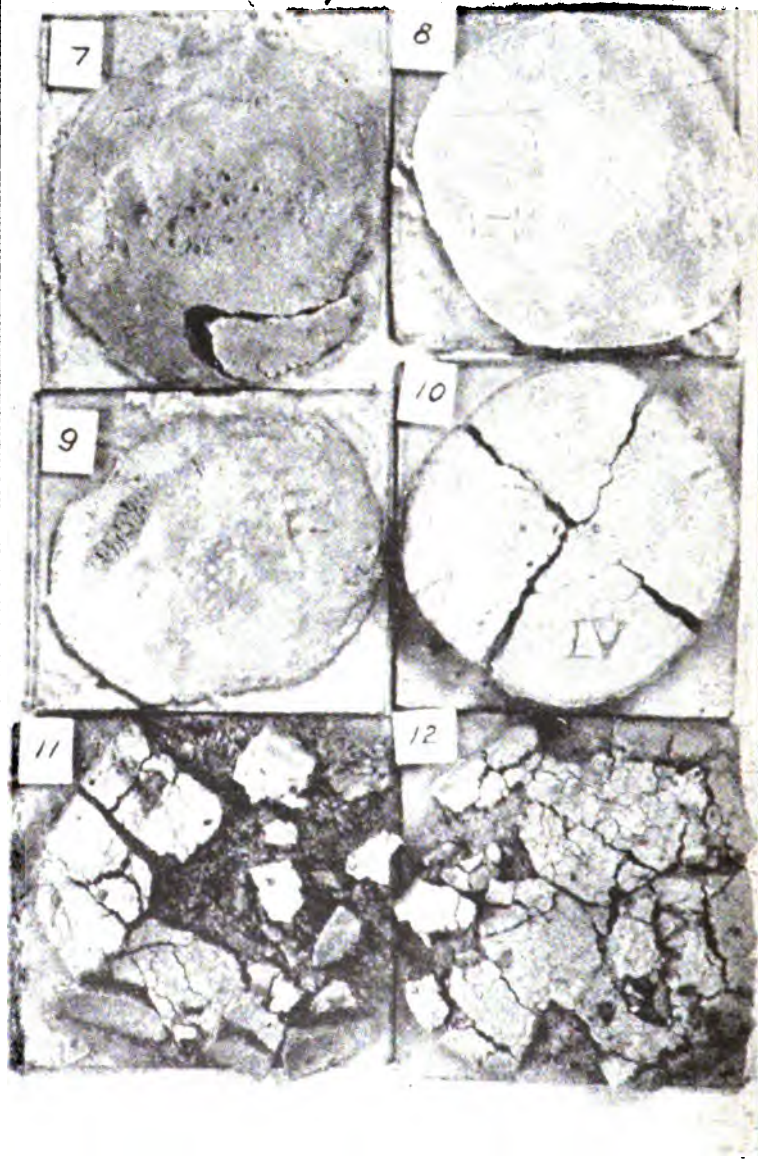
The composition of the clinker produced at some of the higher temperatures was as follows: Total SiO_2 , 21.55; total Al_2O_3 , 9.09; Fe_2O_3 , 2.56; CaO , 63.01; MgO , 2.73; SO_3 , 0.60; total 99.56 per cent.

The molecular ratios in the clinker calculated to the basis of 100 molecules of silica are as follows: SiO_2 , 100; Al_2O_3 , 24.9; Fe_2O_3 , 4.5; CaO , 315.2; MgO , 19.1. The appearance of the clinkers is shown in Plate VI.

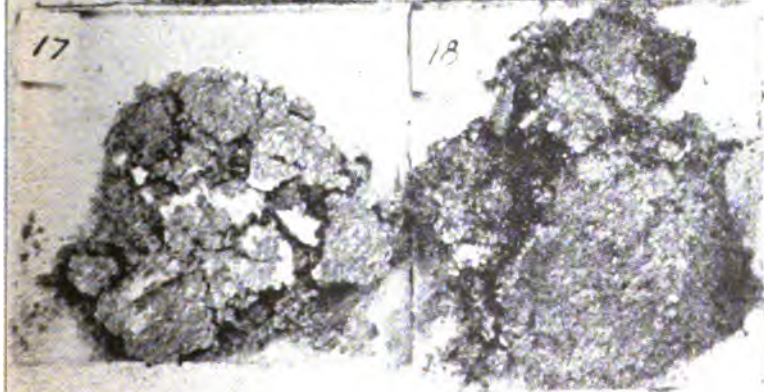
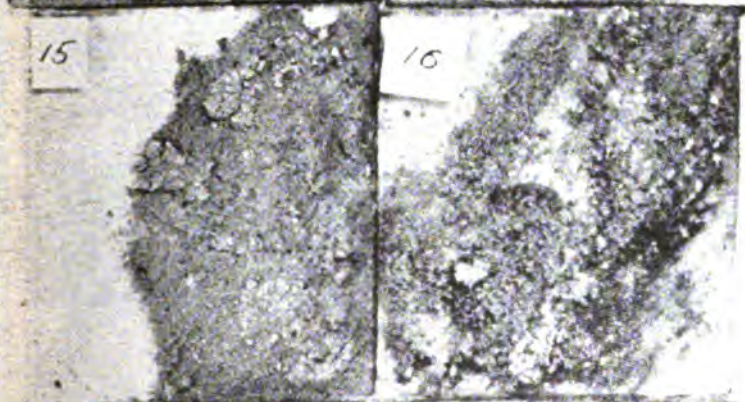
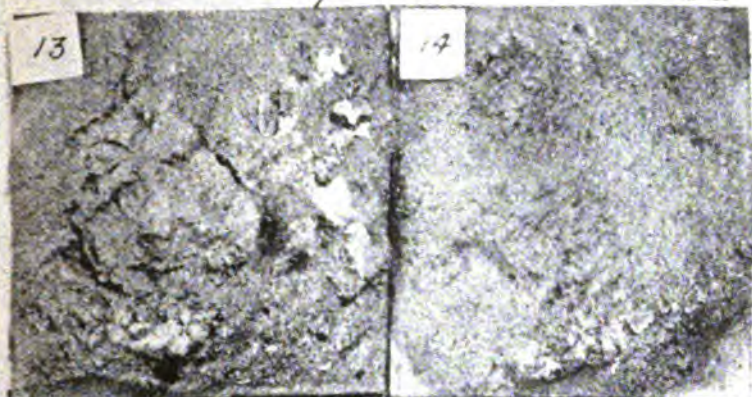
Exp. 104 PLATE II



Exp 104 PLATE III



























Exp. 104 PLATE IV



Exp. 104 PLATE V



Exp. 105 PLATE VII

1 1022° 	2 1049° 	3 1071° 	4 1101° 	5 1124° 
6 1148° 	7 1174° 	8 1198° 	9 1224° 	10 1247° 
11 1281° 	12 1301° 	13 1327° 	14 1352° 	15 1370° 
16 1401° 	17 1425° 	18 1451° 	19 1475° 	20 1501° 
21 1530° 	22 1556° 	23 1582° 	24 1627° 	

Temp. in degrees Cent

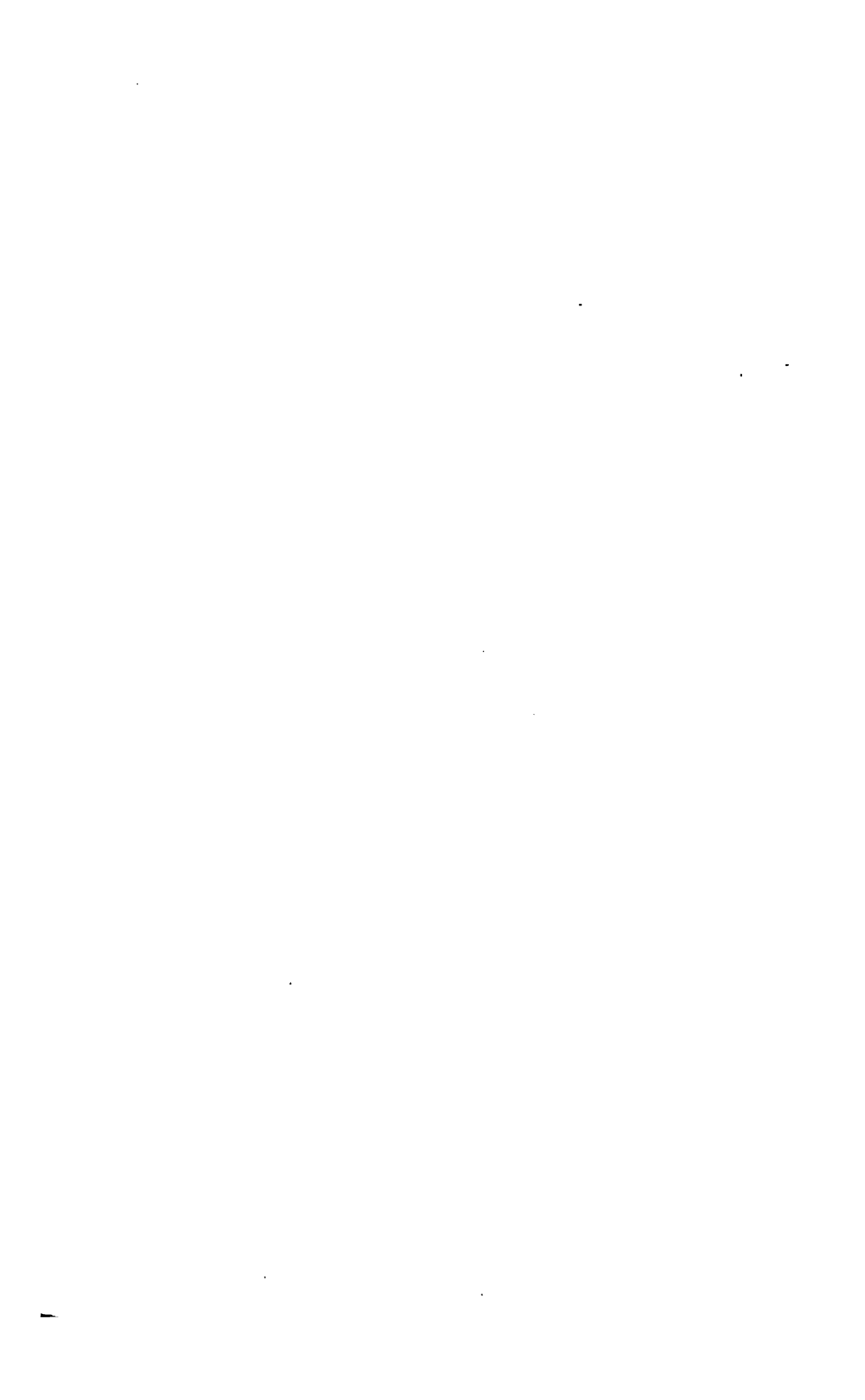


TABLE III, EXPERIMENT 105.

Sample number.	Clinker temperature.	Water. Per cent.	Initial set.		Final set.		Boiling test.	
			Hour.	Minutes.	Hour.	Minutes.	Perfect pat.	quite strong.
1	1022	49	..	11	5	10	"	"
2	1049	53	..	18	7	..	"	"
3	1071	61	..	23	7	20	"	"
4	1101	73	..	39	7	47	Loose from glass, slightly cracked, quite strong.	
5	1124	77	..	27	7	25	Slightly warped, cracked, quite weak.	
6	1148	78	..	7	5	13	Badly warped, cracked, very weak.	
7	1174	77	..	5	4	..	Badly cracked, very weak.	
8	1198	69	..	½	..	16	Badly cracked, warped, very weak.	
9	1224	64	..	½	..	4	" " " "	
10	1247	62	..	½	3	40	" " " "	
11	1281	54	..	1	5	..	Badly warped and disintegrated.	
12	1301	46	..	1	..	46	Very badly warped and disintegrated.	
13	1327	44	..	1	..	29	Very badly warped, cracked, almost completely disintegrated.	
14	1352	40	..	3	..	21	Completely disintegrated.	
15	1378	37	..	3½	..	27	" " " "	
16	1401	33½	..	18	3	15	" " " "	
17	1425	32	..	10	2	22	Badly warped and cracked, almost completely disintegrated.	
18	1451	30	..	14	4	45	Slightly warped, cracked, loose from glass, but quite strong.	
19	1475	28	1	5	4	40	Perfect pat.	
20	1501	27	..	32	4	22	" " " "	
21	1530	28½	..	1	3	53	Perfect pat, sample slightly off color.	
22	1556	26½	..	32	4	..	Perfect pat.	
23	1582	24	..	21	4	..	" " " "	
24	1627	24½	..	10	3	50	" " " "	

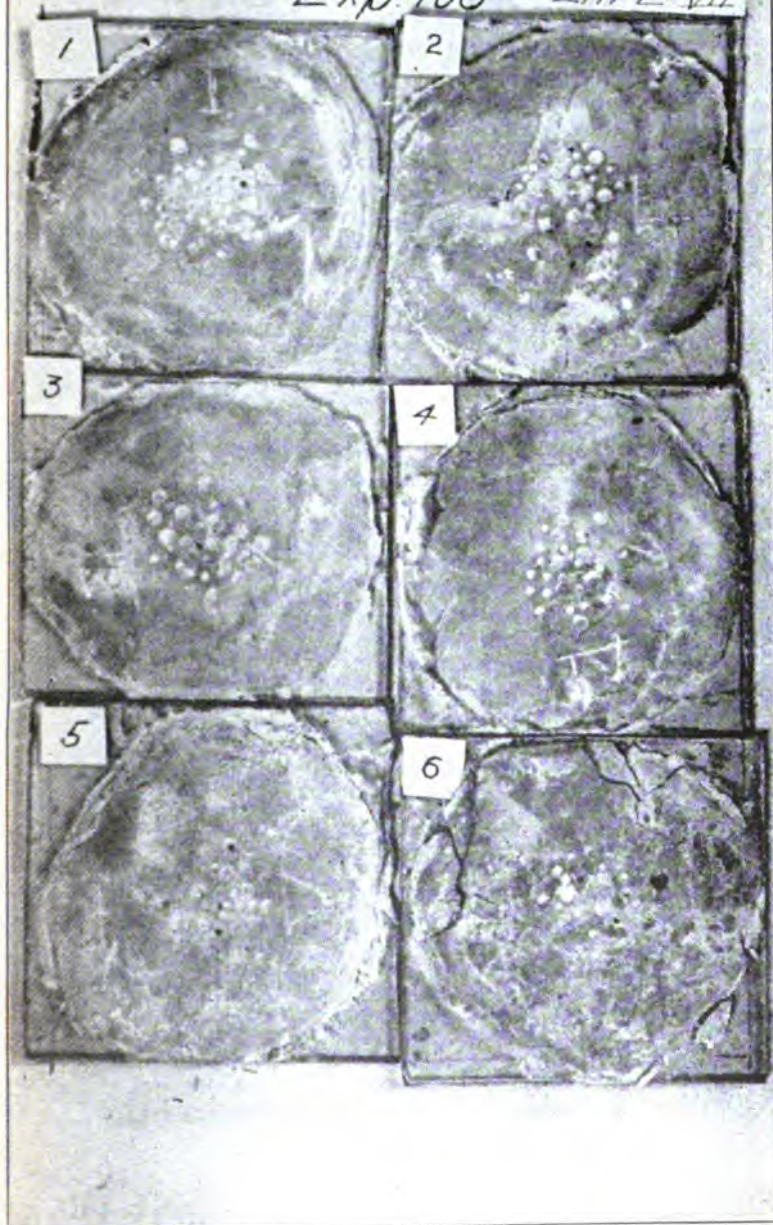
Samples of these clinkers were ground with 1.5 per cent. calcium sulphate (dehydrated gypsum), and determinations of water required for normal consistency, initial and final sets, and boiling tests were made as in the previous experiment. The data obtained from Experiment 105 are summarized in Table III.

The appearance of the pats from Experiment 105 is shown in Plates VII, VIII, IX and X.

In considering the samples of Experiment 105, the conditions of formation of sample No. 21 should be taken into account. Up to sample No. 20 inclusive, the color of the clinker darkened progressively with increase of temperature. Owing to some difficulty with the hydrocarbon burner, the gasoline jet would not draw in sufficient air for complete combustion above 1501°C. , at which temperature No. 20 was burned. When the valve was opened a little wider in order to raise the temperature, a small amount of carbon monoxide was produced in the gas with the result that the clinker became a little lighter rather than darker in color. Oxygen was introduced from the time No. 21 was collected with the result that Nos. 22, 23 and 24 all had the deep blackish brown color characteristic of properly burned clinker. Whether the quick initial set of No. 21 was due to the slight reducing conditions in the furnace at the time of burning, we are not prepared to state positively. It will be noticed that with the exception of No. 21, the time of the initial set, after a perfect hot test was obtained, decreased with increased temperature, but the time between the initial and the final set for these same samples was nearly constant. The influence of the atmosphere within the furnace upon the time of setting as well as upon the other properties of cement, we hope to investigate more closely at a later date.

It was thought that some light might be thrown upon the reactions of clinkering by dissolving, in dilute hydrochloric acid, some of the clinkers produced at temperatures at which there were marked changes in the physical properties of the cement. The first method employed was that usually recommended; that is, three successive boilings for five minutes each with 10 per cent. hydrochloric acid. A number of experiments, however, proved that more complete decomposition could be effected by digestion with hot hydrochloric acid than with successive boilings. If the

Exp. 105 PLATE VII



Exp. 105

PLATE VIII

7

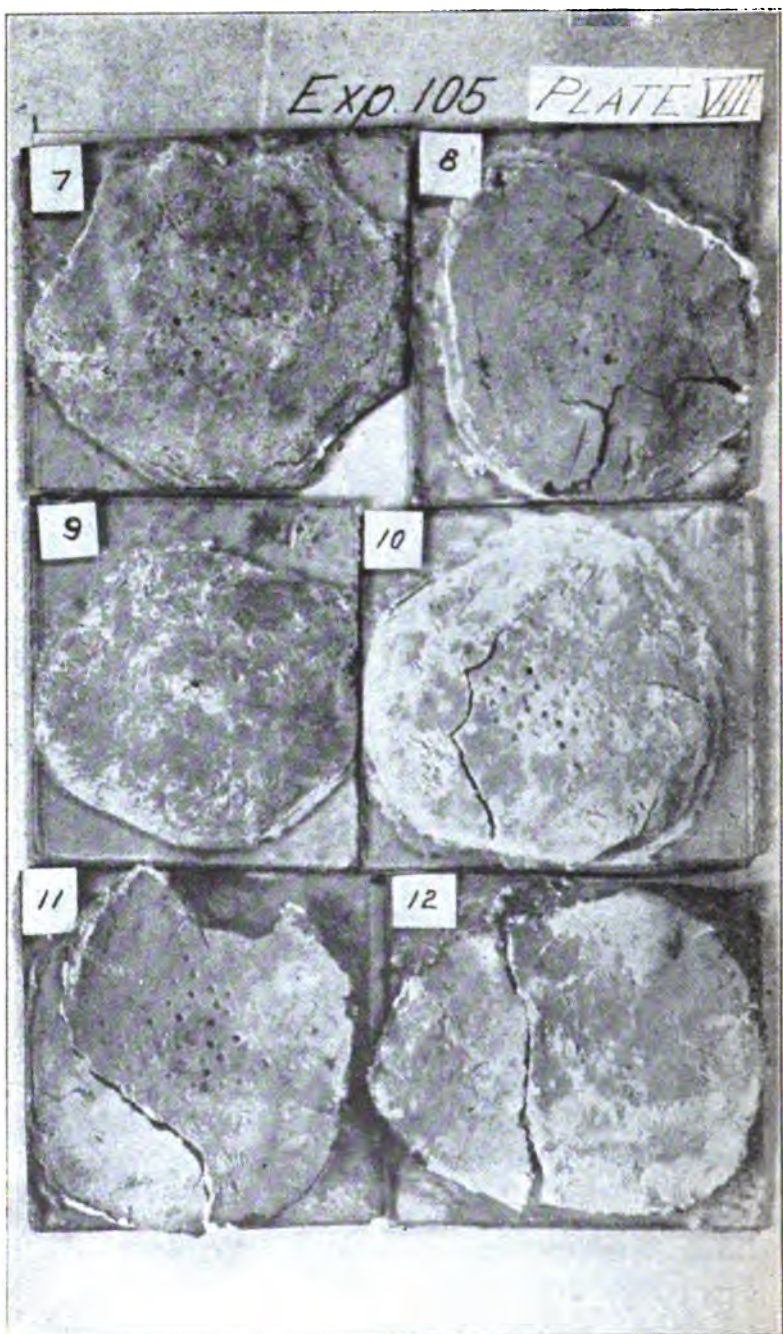
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10

11

12



Exp. 105 PLATE IX

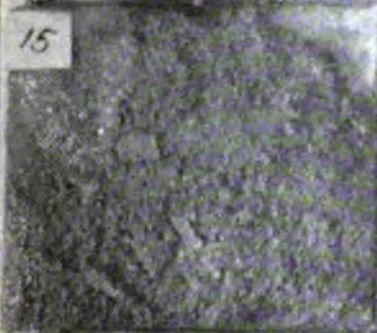
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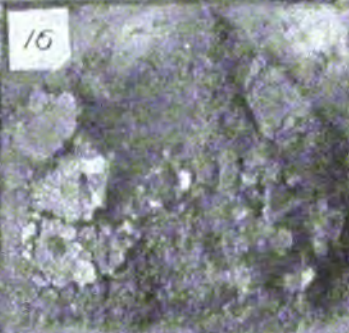
14



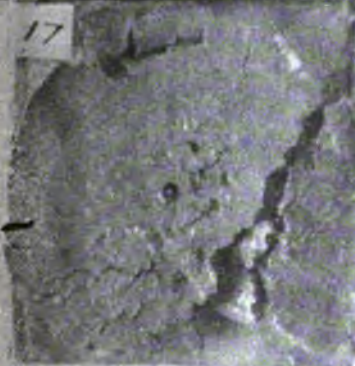
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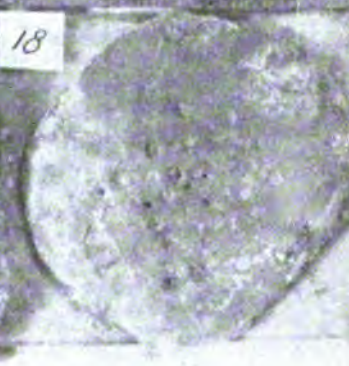
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17



18

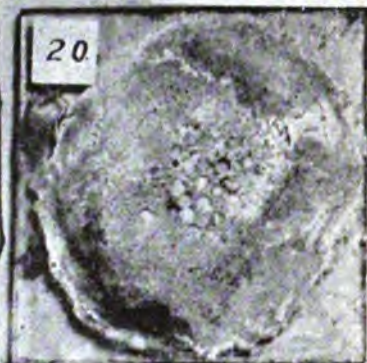


Exp. 105 PLATE X

19



20



21



22



23



24



acid solution containing the cement in suspension is boiled, gelatinous silicic acid seems to deposit on some of the larger particles of cement, thus preventing the acid from effecting complete decomposition. It was found that if 0.5 gram of the cement is placed in 50 cc. of water and this boiled for from two to three minutes, then removed from the hot plate and 5 cc. hydrochloric acid (sp. gr. 1.20) added, and the solution stirred for about five minutes without further heating, the silicic acid set free nearly all remains in solution and a more perfect decomposition is apparently effected than by boiling.

Accordingly, six of the samples were treated in this way. The total silica having been determined, samples of the various clinkers examined were first boiled with water, to which was then added the hydrochloric acid, and after a few minutes' stirring the solution was filtered. The residue, after washing with acidified water until free from soluble salts, was gently ignited and weighed. The difference in weight between this residue and that obtained by the usual method of decomposition, evaporation to dryness, etc., for total insoluble residue, was taken as " SiO_2 soluble in HCl ." The residue insoluble in hydrochloric acid was boiled in a platinum dish with 10 per cent. sodium carbonate, filtered, washed, and weighed. The loss thus obtained was reported as " SiO_2 soluble in Na_2CO_3 ." The residue from the digestion with sodium carbonate was treated with hydrofluoric acid, the loss giving the " SiO_2 by HF ." The final residue was reported as "Residue from HF ." With the exception of No. 1, which gave a loss on ignition of 21.03 per cent., the decomposition of the calcium carbonate of the samples examined was complete. The action of hydrochloric acid, etc., upon the six samples examined is summarized in the following table:

TABLE IV.

Sample number.	Clinker temperature.	SiO_2			Residue from HF .
		sol. in HCl .	sol. in Na_2CO_3 .	by HF .	
1	1022	5.67	1.18	10.67	4.54
6	1148	8.77	0.86	8.34	4.09
9	1224	13.92	1.19	4.09	2.86
14	1352	17.91	3.61	0.28	0.26
19	1475	19.99	1.23	0.42	0.42
24	1625	20.03	1.07	0.50	0.46

Although the results given in Table IV cannot be considered as final and will need confirmation, they indicate one or two rather interesting points.

It will be noticed that the silica, soluble in hydrochloric acid, increases with the increase in the temperature at which the clinker is produced. The silica, soluble in sodium carbonate, however, reaches a maximum in sample No. 14, burned at 1352° . The total insoluble residue after treatment with sodium carbonate, usually reported as "undecomposed silicate," is smallest (0.54 per cent.) in this same sample. The amount of undecomposed silicates seems to increase with rise in temperature above 1352° , and the proportion of silica given off on treating these undecomposed silicates with hydrofluoric acid, is about one-half their weight.

These results would go to indicate that probably all of the original silicates were converted into readily decomposable basic silicates by the time a temperature of 1352° was reached, and that the increased amount of undecomposed silicates found in the high numbers may be due to the more acid silicates left in the magma, from which the tricalcium silicate or other true cement-forming material has separated.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE THEORIES OF INDICATORS.¹

BY JULIUS STIEGLITZ.

Received August 10, 1903.

IN CONNECTION with the use of indicators in the titration of acids and alkalies there are two main questions of theoretical interest: First, what chemical change does the indicator undergo which causes it to change color, and, second, what is the cause of the characteristic differences in sensitiveness shown by such indicators as phenolphthalein and methyl orange towards the various acids and bases—differences which are of the greatest importance in laboratory practice.

Considering first the more interesting question as to the change of color, we find two distinct views held; but only one, the theory of Ostwald, has become generally known and has found a place

¹ See Stieglitz, this Journal, 24, 588 (1902).

and uniform acceptance in every modern text-book examined¹ which discusses the subject at all.² It is extremely probable, moreover, that this theory is wrong in so far as the interpretation of the cause of the change of color is concerned. The other view, growing out of researches with organic dyes and other colored substances, appears to be almost unknown, although work in more recent years is confirming results which had their origin over ten years ago. While most likely wrong in regard to the one question of change of color, Ostwald, in his theory of indicators, has undoubtedly laid down correctly the guiding principles of the proper theoretical treatment of the second, scientifically far more important, question, concerning the varying sensitiveness of the indicators to acids and bases. In this paper, it is proposed to discuss, critically, the two theories concerning the change of color and particularly to develop the relation of the newer interpretation of this phenomenon to Ostwald's fundamental views on the sensitiveness of indicators. It is thought that such a development may remove the main obstacle in the way of the general acceptance of what seems to the author the correct explanation of the color change.

THE CHANGE OF COLOR OF INDICATORS.

The Ionization Theory.—All indicators used with acids and bases, as Ostwald pointed out, are themselves either bases or acids and capable of salt formation. A few, like methyl orange,³ are at the same time both base and acid (amphoter), and able to form salts either with an acid or a base. There is an undoubted intimate connection between this salt formation and the change of color, but what is the real nature of the connection? According to Ostwald's theory,⁴ which has found such wide acceptance, the change of color of an indicator, tersely expressed, is due to a change of its ionic condition. In the case of phenolphthalein, which may be used in illustration, the colorless molecule,

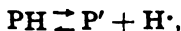
¹ Ostwald's "Lehrbuch der allgemeinen Chemie," 1891, and "Scientific Foundations of Analytical Chemistry," 1900; Walker's "Introduction to Physical Chemistry," 1899; Nernst's "Theoretische Chemie," 1900; Arrhenius's "Electrochemie," 1901; Jones's "Elements of Physical Chemistry," 1902, and "Principles of Inorganic Chemistry," 1903.

² See, however, W. A. Noyes's "Organic Chemistry," published while this paper was being written, and referring to the other, probably correct view.

³ The indicator characteristics of methyl orange are due essentially to its basic character (see below).

⁴ Ostwald: *Loc. cit.*

$\text{OCOC}_6\text{H}_4\text{C}(\text{C}_6\text{H}_4\text{OH})_2$, (I), is supposed to produce the red
 $\text{OCOC}_6\text{H}_4\text{C}(\text{C}_6\text{H}_4\text{OH})\text{C}_6\text{H}_4\text{O}^-$, (II). Phenolphthalein, which appears to be a very weak acid, can indeed be very little ionized in aqueous solution, and the dissociation constant for the condition of equilibrium,



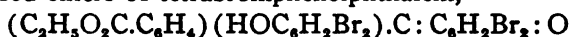
must be so small that a slight excess of hydrogen ions from any acid would be able to suppress almost completely the negative phenolphthalein ions. Its alkali salts, however, would be very highly ionized, like all alkali salts. We have, therefore, coincident with the change of color, a change also of phenolphthalein from the molecular to the ionic condition. It was, perhaps, a perfectly natural, although not a necessary, conclusion that the simultaneous change of ionic condition and color bear the relation to each other of cause and effect. This conclusion was, doubtless, even more readily reached and accepted because Ostwald had just shown,¹ with the aid of the spectroscope, that many of the characteristic changes of color which dry inorganic salts experience on treatment with water are almost certainly due to changes from the molecular form to the differently colored ions, so that solutions of all salts of a given metal like copper show identical absorption spectra when the salts are completely ionized.² In spite of this parallel with inorganic salts and, notwithstanding the striking coincidence mentioned above, on which this theory of the change of color of an indicator like phenolphthalein is based, facts have been known for ten years and new ones have become known more recently, which prove that the change is not primarily due to a change of ionic condition, but to a very important change of constitution of the phenolphthalein molecule when it goes from the colorless into the red condition.

The "Chromophoric Theory."—In view of what chemists have known for over a quarter of a century about the intimate connection between color production and constitution of organic compounds, the explanation that phenolphthalein (I) without a single chromophoric group should become intensely red by forming the ion (II) without any chromophoric group, appeared from the

¹ In the "Lehrbuch," p. 799, the theory of indicators follows immediately the discussion of the color of inorganic salts.

² See, however, Kastle, *Am. Chem. J.*, 16, 326 (1894).

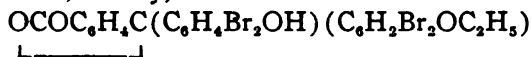
outset as extremely unlikely. As early as 1892, a year after Ostwald's theory was published, Bernthsen¹ made it appear practically certain that whereas phenolphthalein in its colorless solution has the constitution of a lactone, as expressed by (I), its red salts are the salts of a carboxyl acid, not a phenol, and have the constitution.² $(\text{MeOOC.C}_6\text{H}_4)(\text{HOC}_6\text{H}_4)\text{C}:\text{C}_6\text{H}_4:\text{O}$. The strongly chromophoric quinoid complex $(:\text{C}_6\text{H}_4:\text{O})$ gives us an explanation of the production of intense color, which is entirely adequate, in view of the general laws governing color in organic compounds. The sodium salt is, no doubt, incidentally ionized in solution, but that this ionization is merely a coincidence and not a cause is established by the fact that the solid, dry, non-ionized silver salt is also intensely colored (violet). Other strong proof that the view first presented by Bernthsen is the correct one, lies in the fact that Nietzki and Burckhart³ have prepared colored, non-ionized ethers of tetrabromphenolphthalein,



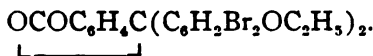
and



with quinoid molecules, and colorless lactoid ethers, isomeric with the colored one, namely,

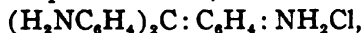


and

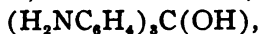


In the absence of the chromophoric quinoid group, color is also absent, but the question of ionization has no effect at all on the matter of color or absence of color.

Similarly, it has long been known that the intensely colored salts of the rosaniline series of dyes are quinone derivatives, *e. g.*, the hydrochloride of pararosaniline,



and that the corresponding free base is more or less rapidly converted into the isomeric, colorless carbinol,



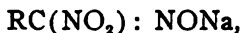
the color disappearing again with the quinone complex. The

¹ *Chem. Ztg.*, p. 1956 (1892). *Vide also Friedländer: Ber. d. chem. Ges.*, 26, 172, 2258 (1893).

² The lactone ring is saponified very readily by alkalis, as are lactones in general.

³ *Ber. d. chem. Ges.*, 30, 175 (1897).

difference between the behavior of phenolphthalein and rosaniline, as will be shown, is essentially a difference in the speed of the change of constitution. More recently, Hantzsch¹ has shown that, in general, the change of colorless organic compounds into highly colored salts is invariably accompanied by a modification of the constitution affecting a chromophoric group. Reference need only be made to the formation of red salts,



from the colorless nitrolic acid,



THE CHANGE OF COLOR OF INDICATORS SHOWING TWO COLORS.

The Ionization Theory.—Turning to the consideration of a second kind of indicators, such as methyl orange and litmus, which change from one color to another, we again find the two theories confronting each other. According to Ostwald's views,² as slightly modified by Küster,³ the yellow color of methyl orange in alkaline solution is due to the formation of an intensely yellow, negative ion,



methyl orange, which is amphoteric, behaving in this case as an acid. In acid solution, we have an ion which carries both a negative and a positive charge,



and which is said to have a not very intense red color. The difference between the two colored substances is supposed to be simply one of ionization; both are supposed to have essentially the same chromophoric complex (the azo groups, $\text{N} : \text{N}$), but different electric charges.

The "Chromophoric Theory."—In view of what has been explained above as to the change of constitution and of chromophoric complexes attending the change of phenolphthalein, the rosanilines, etc., from a colorless to a colored condition, we are justified in questioning the adequateness of the ionization explanation of the change of color, also, of bicolored indicators like methyl orange. We may ask whether analogous, constitutional and chromophoric changes of the molecule of methyl orange do not

¹ *Ibid.*, 32, 583, 3085 (1899), etc.

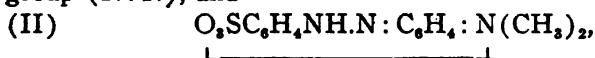
² "Scientific Foundations of Analytical Chemistry."

³ *Ztschr. anorg. Chem.*, 13, 135 (1897); *Vide* Nredig: *Ztschr. Elektrochem.*, 6, 33 (1899).

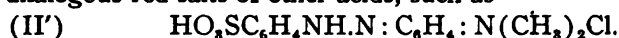
accompany its transition from yellow to red, and vice versa. As a matter of fact, for reasons quite distinct from the sole question of color, chemists have for a number of years been seriously divided as to the true constitution of dyes of the class of methyl orange (amino and hydroxyazobenzene dyes). There are two possible constitutions for methyl orange:



which represents an aminoazobenzene with a chromophoric azo group ($\text{N}:\text{N}$), and



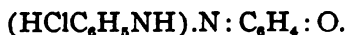
the inner salt (sulphonate) of a phenylhydrazone of an iminoquinone, containing the chromophoric quinoid group ($:\text{C}_6\text{H}_4:$). It seems extremely probable that in alkaline solutions we have yellow, metal salts of methyl orange of the constitution (I), with the azo group, and, in acid solution, red salts of the quinoid constitution (II) or, in the presence of an excess of acid, the perfectly analogous red salts of other acids, such as



The change of color would then be attended by a profound change of chromophoric complexes. Aside from the general considerations of analogy to phenolphthalein and other dyes, and of agreement with the general laws governing color in organic compounds, the chief support for this "chromophoric theory" of the change of color of bicolored indicators is found in the fact that for hydroxyazobenzene, which structurally is entirely analogous to methyl orange, Hantzsch¹ has recently proved that in alkaline solutions it is, indeed, the salt of an azophenol,



but in neutral and acid solutions a phenylhydrazone of quinone, *e. g.*,



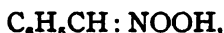
The dry sodium salt is orange, the dry hydrochloride a deep purple-red. With the change of constitution we have, therefore, again a marked change of color.

THE CHANGE OF COLOR AND OF IONIZATION A COINCIDENCE.

Results of the last ten years in the field of organic chemical research, such as the work of Nef on the salts of acetoacetic and

¹ *Ber. d. chem. Ges.*, 32, 590, 3089 (1899).

malonic ethers,¹ and of Hantzsch on pseudo-acids and bases, enable us to understand also very readily why there should be this striking coincidence between the change of color of indicators and the change of the ionic condition without any strictly causal relation between the two facts. The coincident is simply due to the fact that many organic acids, and among them indicators that are acids, are extremely unstable in the form of *free acids*, and readily suffer a change of constitution to closely allied, isomeric (tautomeric) substances, which are no true acids (not ionized). Analogous relations are known to exist for many organic bases. The *salts*, however, of such acids or bases are stable, whether in solution (ionized) or dry (non-ionized). Thus nitrophenylmethane is known in two forms;² isonitrophenylmethane,



a rather strong acid, which is precipitated when the solutions of its salts are rapidly and strongly acidified, but which changes gradually and spontaneously to a stable, neutral isomer, nitrophenylmethane,



In other cases of this kind, the isomerization is instantaneous.

Such a substance, to be serviceable as an indicator, must suffer isomerization from the acid (or basic) condition to the pseudo (neutral) condition or vice versa, practically *instantaneously* and the isomerization *must also affect a chromophoric group*. In the case of phenolphthalein, which may again serve in illustration, we must have a true acid form,



from which the colored metallic salts are derived, but which in

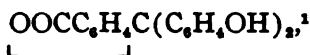
¹ Vorländer (*Ber. d. chem. Ges.*, 36, 268 (1903)), having proved malonic ether to be a true weak acid in aqueous solution, supposed that this fact proves also that the salts of malonic ether have the constitution $\text{MeCH}(\text{COOR})_2$ and not $\text{ROOC}\cdot\text{CH}:\text{C}(\text{OMe})\text{OR}$, as advocated by Nef. As a matter of fact, the evidence merely shows that malonic ether is somewhat ionized in aqueous solution and a very weak acid. The assumption that an oxygen acid, $\text{ROOC}\cdot\text{CH}:\text{C}(\text{OH})\text{OR}$, must be a strong acid is entirely unwarranted; but, moreover, the important fact is left entirely out of consideration that in an aqueous solution, two forms of malonic ether would be in equilibrium with each other, *viz.*,



If there were very little of the latter acid found present, malonic acid would appear to be a very weak acid, even if the acid form ionized quite easily (see below). The results of Vorländer are, therefore, evidence neither for nor against Nef's views as to the constitution of the salts, and taken in connection with Hantzsch's work on pseudo-acids rather confirm Nef's conclusions.

² Hantzsch: *Ber. d. chem. Ges.*, 29, 699, 2251 (1896).

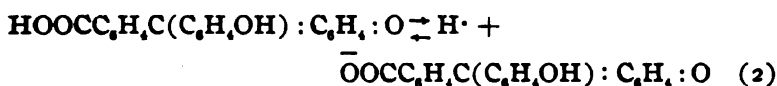
the free acid condition must go, practically, instantly over into the colorless lactoid form,



the hydrogen atom, H^* , suffering a change of position. The lactone is the more stable of the two isomers, belonging, as it does, to the most stable class of lactones, the γ -lactones. However, in an aqueous solution of phenolphthalein we must have, as in the case of all such tautomeric substances, a condition of equilibrium between the lactoid and quinoid forms:



The condition of equilibrium favors the lactoid form, since the solution is colorless, and only minimal quantities of the quinoid acid can be present. This trace of quinoid acid is ionized and in equilibrium with its ions:

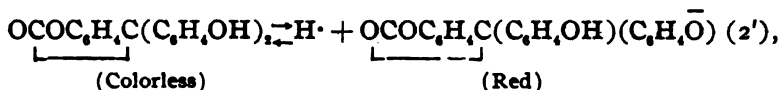


The addition of an alkali causes the hydrogen ions (equation 2) to disappear; more of the quinoid molecules (equations 1 and 2) must be ionized to preserve equilibrium and the quinoid molecules, in turn, be reproduced from the lactoid (equation 1) as fast as the former are converted into the salt. The effect of the alkali, therefore, is to suppress the colorless lactoid isomer by converting the unstable, free quinoid acid into its stable quinoid salt, which is colored red and is incidentally ionized. That it is only a question of stability of the salt and not of ionization is proved by the fact that the dry salts are as intensely colored as the solution. The case is obviously entirely analogous to that of carbonic acid, whose neutral alkali salts, the carbonates, whether ionized in solution, or non-ionized in a dry state, are so very much more stable than the free acid. In fact, in both cases, the dry, non-ionized condition is rather more favorable to stability and, therefore, in the case of phenolphthalein, to the maximum formation of color, since in consequence of the ionization in aqueous solution we have hydrolysis and a reversal of equations (1) and

¹ It is possible that the unstable isomer, the true carboxylic acid, will some day be isolated; but this is not at all essential for the theory, as analogous unstable isomers, such as isonitrophenylmethane, have been isolated and their spontaneous change studied.

(2) for phenolphthalein and an analogous change of the carbonates.

The equilibrium equations (1) and (2), as just developed, enable us to put the two theories of the cause of the change of color of indicators briefly, thus: Ostwald's theory takes an equation analogous to (2), *viz.*,



alone into account, ascribing the change of color to the shifting of equilibrium according to (2'); the "chromophoric theory" takes both equations, (1) and (2), into account and ascribes the *change of color* to the shifting of equilibrium according to (1).

THE SENSITIVENESS OF INDICATORS.

This condensed contrast of the two theories enables us to proceed to the second question raised in the opening paragraph of this paper, to the question as to the different degrees of sensitiveness of the various indicators to weak acids and bases.

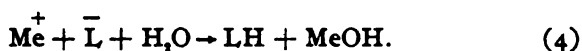
In this, the more important of the two questions raised, Ostwald has brilliantly laid the foundations for a correct theoretical interpretation and practical application of the varying phenomena, and we need only consider in what relation the new interpretation of the cause of the change of color stands to his views on the sensitiveness of indicators.

The Ionization Theory.—According to Ostwald, the indicators, as acids and bases, take part in the changes of chemical equilibrium in the solution by forming salts and are subject to the general laws governing equilibrium and notably to that of mass action. The sensitiveness of an indicator, consequently, must depend chiefly on the numerical size of its ionization constant as an acid or base. For instance, according to (2')

$$C_H \times C_L = K \times C_{LH}, \quad (3)$$

if C_H , C_L , and C_{LH} represent, respectively, the concentrations of the hydrogen ions, the complex organic negative ions and the non-ionized molecules of an acid indicator, and K its ionization constant according to Ostwald's dilution law for organic acids. If, as in the case of phenolphthalein, the colored substance is the complex negative ion, the formation and intensity of color would

be measured by C_L . As explained above, by the suppression of the hydrogen ions (C_H) and the formation of metal salts, which are largely ionized, C_L would become very large. Now, if the ionization constant K is exceedingly small and the indicator, therefore, a very weak acid, it cannot be sensitive to very weak bases, because the nearer the dissociation constants of base and acid approach that of water itself, the less readily are salts formed; water prevents their formation by hydrolysis according to the well-known equation:



In the same way, the smaller the dissociation constant K or the weaker the indicator is as an acid, the more sensitive and, therefore, the more serviceable will it be in the titration of ordinarily weak acids, such as oxalic, acetic and carbonic; the small excess of hydrogen ions formed by these acids would be sufficient to drive the indicator out of its colored salts into the colorless molecules, since C_L grows smaller, according to (3), as C_H grows larger, and it does so the more rapidly the smaller K is.

By the same process of reasoning, it would follow, vice versa, that an indicator which is a moderately strong acid with a large dissociation constant, as methyl orange was supposed to be, or one which is a very weak base, with a very small dissociation constant as a base, as methyl orange really is,¹ would be an excellent indicator for strong or weak bases, but a very poor one for weak acids.

These conclusions, as developed from Ostwald's statements, agree in the main with the facts as far as they are known. Observations have been chiefly of a qualitative nature, and quantitative measurements of the dissociation constants of our most important indicators are extremely desirable,² but there is no reason to expect that they will modify in any way Ostwald's views which have just been described.

The "Chromophoric Theory."—The above views are based, however, on Ostwald's theory as to the change of color, briefly, for phenolphthalein, on equation (2'). But it is almost certain that this part of the theory is wrong and that the two equations, (1) and (2), express the changes in an indicator, and (1) in par-

¹ As explained below, the value of methyl orange as an indicator is due rather to its weak basic functions than to its acid character.

² *Vide Bredig: Loc. cit.*

ticular expresses the cause of the change of color. A brief consideration will show that this new view does not modify, in any fundamental respect, the result of the application of the laws of chemical equilibrium to the indicators, but simply introduces one or more new constant factors into the final equilibrium equation, factors which are rather helpful than otherwise in the interpretation of the facts.

Using phenolphthalein again as an illustration, we have two conditions of equilibrium occurring simultaneously in solution. First, according to equation (1), (p. 1119),

$$C_{QH} = k \times C_{LH}, \quad (5)$$

if C_{LH} and C_{QH} represent the concentrations of the lactoid and quinoid forms of phenolphthalein and k is a constant. Again for equation (2), (p. 1119), we have

$$C_Q \times C_H = K' \times C_{QH}, \quad (6)$$

if we express the concentrations of the negative quinoid ions and of the hydrogen ions by C_Q and C_H , that of the undissociated quinoid molecules again by C_{QH} , and the ionization constant of Ostwald's dilution law by K' .

Combining (5) and (6) we have:

$$C_Q \times C_H = k \times K' \times C_{LH} \quad (7)$$

or

$$C_Q \times C_H = K'' \times C_{LH}. \quad (7')^1$$

This is the same form of equation as developed above for the sensitiveness of the indicators (equation 3), with this simple difference that in equation (3) the constant K is only the ionization constant, in equation (7'), K'' is the product of the true ionization constant K' of the quinoid acid and the stability constant k of the two tautomeric forms of phenolphthalein. Equation (7') tells us, therefore, that such an acid as phenolphthalein is in its effect only as strong an acid as the joint action of ionization and possibility of molecular existence in solution make it. Its tend-

¹ In this expression, for an aqueous solution of phenolphthalein, C_Q and C_H are not equal to each other, as hydrogen ions are formed not only by the carboxyl group of the quinoid acid but also by its phenolhydroxyl group as well as by the two phenolhydroxyl groups of the lactoid acid. The effect of this increase of hydrogen ions is to make phenolphthalein, as indicator, react as a still weaker acid than it otherwise would, that is, it is less sensitive to alkalis, more sensitive to acids. Thus phenolphthalein is affected favorably in the very direction in which it is of particular value as an indicator. A most instructive quantitative study of similar relations has been carried out for carbonic acid by H. N. McCoy, *Am. Chem. J.*, 29, 437 (1903).

ency to produce the red color is measured by the same constant K'' . Entirely analogous relations and equilibrium equations, it may be added, exist for ammonium hydroxide, which also is unstable in solution.¹

It is obvious from a comparison of equations (7') and (3), that all of the conclusions as to sensitiveness which were based on equation (3) apply equally well to the new equation (7'). The substitution of (7) for (3) shows us further, however, the great importance of the stability constant k , for the smaller k is the more difficult will it be to obtain the quinoid acid and its salts, to which the red color of the alkaline phenolphthalein solution is due, and consequently the less sensitive will the indicator be to alkalis. It is very probable, indeed, that phenolphthalein in its quinoid form with a carboxyl group is not such a very weak acid in itself, but the minute quantities in which it is able to exist in the free state make it appear and react as such.

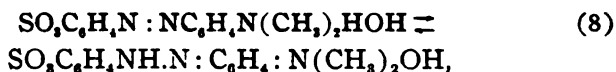
But a still more important conclusion concerning indicators can be drawn from the substitution of equation (7') for (3) and the introduction of the stability constant k into the final equilibrium equation. Whereas changes involving only new conditions of equilibrium of ions always take place practically instantaneously (equation 6), reactions involving the transformation of one isomer into another (equation 5) show the widest range of difference as regards the velocities of the changes. The constant k of this equation (5), as is well known, is merely the ratio of the velocities of the two opposite reactions; the same ratio may be the result of two exceedingly great or two very small velocities. Now the velocities of change for serviceable indicators, no matter what their ratio is, must be exceedingly great in either direction, and practically of the order of the velocity of ionic changes. It is very probable that in the case of the indicators actually used the velocities are not only very great in both directions, but are increased by the catalytic action of hydroxyl and hydrogen ions² in such a way that complete equilibrium, according to (5) and (6), is reached instantaneously. This consideration shows us wherein an indicator differs from other intensely colored sub-

¹ Kohlrausch: *Wied. Ann.*, 26, 197 (1885); Ostwald: *J. prakt. Chem.* (2), 33, 358 (1886), and *Ztschr. phys. Chem.*, 2, 36 (1888); Hantzsch: *Ibid.*, 30, 258 (1899).

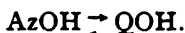
² Cameron's observation (*Am. Chem. J.*, 23, 477 (1900)) that the red color of phenolphthalein is rather slowly discharged by carbonic acid may be the result of such an action. His own interpretation is surely wrong.

stances, such as rosaniline, which shows as striking color changes as phenolphthalein; it is intensely red in solution, colorless (as carbinol) in alkaline solution, but the transformations are much too slow,¹ at ordinary temperatures, to make rosaniline available as an indicator in acidimetry.²

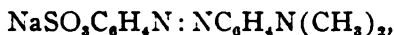
For methyl orange, which exhibits a sensitiveness in extreme contrast to that of phenolphthalein and which, incidentally, is a bicolored indicator, relations exist which are entirely analogous to those developed above for phenolphthalein. It is always used in neutral solution in the form of a sodium salt and it is in this sensitive neutral solution that we must have a condition of equilibrium between the two tautomeric forms of methyl orange, which were previously discussed (p. 1117). It can best be expressed as follows:³



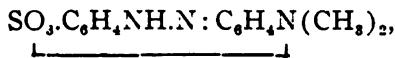
or



The azo derivative on the left hand of the equation is yellow, as the solid sodium salt, which can only be



is yellow; the quinoid form on the right hand is red, for instance, in the form of the solid free sulphonate,



as explained above.

¹ It is also too strong a base to be very sensitive.

² NOTE.—In his work on the pseudo-acids and -bases, Hantzsch uses the method of comparing the affinity constant, for instance, of an acid as determined from the measurement of the hydrolysis of its salt, with the affinity constant as ascertained by conductivity measurements in the aqueous solution of the pseudo-acid and decides, on the basis of the great differences in the values obtained, that the free acid must be a different substance (isomeric or tautomeric) from the acid in the salt. This conclusion is perfectly justified and the method an admirable one. But it is never clearly emphasized by Hantzsch—perhaps inadvertently—that such differences can result only if measurements are made before a final condition of equilibrium can possibly have been reached in all the solutions used. Equation (7'), as used in the text, rests, therefore, less on quantitative work done with tautomeric substances than on the experimental work of Kohlrausch (*Loc. cit.*) and Ostwald (*Loc. cit.*) on the ionization of ammonium hydroxide and on that of Bodländer (*Ztschr. phys. Chem.*, 35, 32) and McCoy (*Loc. cit.*) on carbonic acid as well as on the laws of chemical equilibrium.

³ The sulphonate group, SO_3Na , is ionized and has absolutely nothing to do with the color changes, as was at first supposed; dimethylaminosobenzene may be used in place of its sulphuric acid derivative, methyl orange. *Vide* Bredig: *Loc. cit.*

If we represent the concentrations in the usual way, we obtain from (8) the equilibrium equation

$$k \times C_{A_{2}OH} = C_{QOH}. \quad (9)$$

As the solution is yellow, the second quinoid form can only be present in very small quantities and the stability constant k must be exceedingly small.

The red quinoid form is also ionized as an ammonium base, according to



We have, then,

$$C_Q \times C_{OH} = K \times C_{QOH}, \quad (11)$$

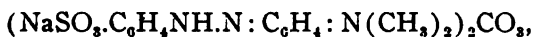
and combining (9) and (11),

$$C_Q \times C_{OH} = k \times K \times C_{A_{2}OH}, \quad (12)$$

$$C_Q \times C_{OH} = K' \times C_{A_{2}OH}. \quad (12')^1$$

This is the same form of equation as was developed above for phenolphthalein (equation 7 and 7'), only we are dealing in this case with a base rather than with an acid. The ion Q and its salts are red and the red color of the acid methyl orange solution depends on the presence of Q and its development is subject to the equilibrium equation (12) or (12').

The whole behavior of the red, quinoid form of methyl orange (its sodium salt) is that of a *very weak* base, analogous to that of dimethylaminoazobenzene² or to the sodium salt of aminoacetic acid.³ It does not form salts readily with weak acids, such as carbonic and acetic acids; the red carbonate,



is practically completely hydrolyzed and incapable of existence, the liberated base reverting, according to (8) and (9), to the stable yellow isomer. That is why methyl orange is not a sensitive indicator for weak acids. As a very weak base, it will be driven readily out of its red salts by other bases, even weak ones, and the free, red base will revert again, according to (8) and (9), to the yellow form, the result being that methyl orange is an ex-

¹ As the amino group of the azo form is basic and forms some hydroxyl ions, C_{OH} is somewhat larger than C_Q in an aqueous solution. This fact, in the same way as explained above for phenolphthalein, favors the sensitiveness of methyl orange to weak bases, its most important characteristic.

² Bredig: *Loc. cit.* Vide, however, Ostwald: *Loc. cit.*, and Küster: *Loc. cit.*

³ Lengfeld and Stieglitz: *Am. Chem. J.*, 18, 516 (1893).

cellent sensitive indicator for weak bases. Accordingly, K' , of equation (12'), must have a very small value, of the order of K'' for phenolphthalein in equation (7'). As the ionization constant K (equation 11) of the quaternary ammonium hydroxide must be a rather large one, the very small value of K' is evidently due to the exceedingly small size of the stability constant k , which is shown, qualitatively at least, by the color of the neutral methyl orange solution.

Our two most valuable indicators, phenolphthalein and methyl orange, which form an extreme contrast, do so as a very weak acid and a very weak base, respectively, in their *quinoid* (red) forms, as shown in equations (7') and (12'); and their weakness is due in largest measure to the *instability* of the quinoid isomers in the form of free acid or free base, respectively.

These considerations give us a complete survey of the chemistry of the different sensitiveness of our two most important indicators on the basis of the conclusions reached in the first part of this paper that the color change must be primarily due to a change of constitution involving a chromophoric complex. An experimental determination of the constants and verification of these views would be very important.¹ They rest, so far, on the work of Bernthsen, Nietzki, and Burckhardt on the phenolphthaleins; on Hantzsch's investigation of the pseudo-acids and -bases, and on the quantitative study of the equilibrium conditions of ammonium hydroxide and of carbonic acid in solution, as quoted above. An experimental study of the peculiarities of indicators, such as the disappearance of the color of phenolphthalein in the presence of a large excess of alkali, would also be profitable and the quinone complex, with its well-known reactivity, would probably be found to be the seat also of this change.²

In conclusion, in connection with the discussion of the sensitiveness of our indicators, too much emphasis cannot be laid on the fact that the lack of sensitiveness of phenolphthalein in laboratory practice in the titration of a weak base like ammonia or of methyl orange in the titration of a weak acid like acetic acid is

¹ Bredig (*Loc. cit.*) has announced an experimental study of methyl orange from Ostwald's point of view, and Dr. H. N. McCoy, of this laboratory, in connection with his work on the affinity constants of carbonic acid, has taken up the determination of the affinity constant of phenolphthalein. The author feels obliged to refrain from pursuing his subject experimentally until these researches are completed.

² The colorless solution probably contains the salt $\text{KO}_2\text{C}_6\text{H}_4\text{C}(\text{OH})(\text{C}_6\text{H}_4\text{OK})_2$. The corresponding triacetate of aurine, $\text{C}(\text{OH})(\text{C}_6\text{H}_4\text{OC}_2\text{H}_5\text{O})_3$, is known and is colorless.

ultimately due chiefly to the fact that a weak base or a weak acid is very much weaker (less ionized) in the presence of its own salts than in pure aqueous solutions.¹ Phenolphthalein will readily show the presence of 0.01 cc. N/10 free ammonia in 100 cc. of pure boiled water, to which only 1 milligram of phenolphthalein has been added. But in titrating ammonia with N/10 hydrochloric acid, very long before all but that small amount has been neutralized, the red color of phenolphthalein disappears, owing to the formation of ammonium chloride. The isothermic equation for ammonium hydroxide is

$$C_{\text{NH}_4} \times C_{\text{OH}} = k \times C_{\text{NH}_3}$$

in which C_{NH_4} , C_{OH} , C_{NH_3} represent the concentrations of the ammonium ions, the hydroxyl ions and the non-ionized ammonia, and k ($= 1:53,750$)² is the ionization constant. It shows how readily the hydroxyl ions must disappear when an easily ionized salt like ammonium chloride is added to a solution of ammonia. A striking insight into the matter is obtained from the result of the following calculation, made with the aid of the isothermic equation and its known constant and of the known degrees of dissociation of solutions of ammonium chloride: If 10 cc. normal ammonium hydroxide are half neutralized by 5 cc. normal hydrochloric acid, the resulting solution, instead of being one-half as effective as a base, as it would have been if sodium hydroxide had been used, contains very nearly only one-hundredth as many hydroxyl ions as the original solution and is, therefore, only one-hundredth as effective as a base. The same result would be attained if to 10 cc. normal ammonium hydroxide 0.32 gram solid ammonium chloride ($= 6$ cc. normal ammonium chloride) is added in place of all the acid. In other words, in these concentrations ammonia is weakened fifty times more by the neutral salt ammonium chloride than by the hydrogen ions (in their neutralizing effect) of a nearly equivalent³ amount of hydrochloric acid. Analogous relations hold for the neutralizing of acetic acid by sodium hydroxide, the affinity constant of acetic acid ($1:55,000$) being nearly the same as that of ammonia.

¹ Arrhenius: *Ztschr. phys. Chem.*, 2, 287 (1888); Klüster: *Ztschr. Elektrochem.*, 4, 110 (1897); Stieglitz: *Am. Chem. J.*, 23, 476 (1900).

² Kohlrausch: *Loc. cit.*; Ostwald: *Loc. cit.*

³ Equivalent to the ammonium chloride.

CHICAGO, April, 1903.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 76.]

**THE BEHAVIOR OF CERIUM, LANTHANUM, NEODYMIUM,
PRASEODYMIUM, THORIUM AND ZIRCONIUM
TOWARD ORGANIC BASES.¹**

BY BURT LAWS HARTWELL.

Received August 18, 1903.

AN INVESTIGATION along these lines seemed to promise well because of the success which Jefferson² met while prosecuting a similar study with a limited number of aromatic bases. It was hoped that some organic base would be found, among the large number to be tried, which would lead to the separation of thorium and zirconium, or, failing in this, that a method would be disclosed by which these two elements could be separated from cerium, lanthanum, neodymium and praseodymium.

Large quantities of thorium and zirconium nitrates were prepared from the mineral thorite and zircon. Numerous qualitative tests were made and the solvents for the bases were, in most cases, water and alcohol, or mixtures of these two, depending upon the solubility of the base. In some instances ether was added to advantage. Alcohol, above a certain strength, precipitated the thorium and zirconium nitrate solutions, so that this point had to be constantly considered during the testing. The salt solution was usually added in small quantities at a time to the solution containing a liberal amount of the organic base. Heat was applied, if precipitation did not occur in the cold. The solutions were not permitted to stand for long periods, as it was thought that differences which did not manifest themselves readily, under ordinary conditions, would scarcely indicate the probability of practical quantitative separations.

The bases studied in this investigation were obtained from Kahlbaum. Those employed by Jefferson³ were usually omitted here.

REAGENTS WHICH PRODUCED NO PRECIPITATE WITH SALTS OF ANY
ONE OF THE SIX ELEMENTS.

Benzylaniline.

p-Nitraniline.

Dimethylnitrosamine.

p-Nitrophenylhydrazine.

¹ From author's thesis for the Ph.D. degree.

² This Journal, 24, 540.

³ *Loc. cit.*

Dipropylnitrosamine.	Piperine.
<i>m</i> -Nitraniline.	Succinimide.
<i>o</i> -Nitraniline.	Tetranitromethylaniline.
<i>o</i> -Chloraniline.	

REAGENTS WHICH CAUSED PRECIPITATES WITH SALTS OF ALL SIX
OF THE ELEMENTS.

Allylamine.	Isodibutylamine.
Benzylmethylamine.	Monoamylamine.
Bornylamine.	Monethylamine.
Camphylamine.	Monomethylamine.
Diamylamine.	Monopropylamine.
Dibenzylamine.	Neurine.
Diethylamine.	Normal butylamine.
Dimethylamine.	Normaldibutylamine.
Dipropylamine.	Propylenediamine.
Ethylenediamine.	Tetrethylammonium hydroxide.
Heptylamine.	Tetramethylammonium hydroxide.
Hexylamine.	Triethylamine.
Isobutylamine.	Trimethylamine.
Isotributylamine.	Tripropylamine.

REAGENTS WHICH PRECIPITATED ONLY THORIUM AND ZIRCONIUM.

Benzidine.	Isoquinoline.
<i>m</i> -Bromaniline.	α -Picoline.
<i>p</i> -Bromaniline.	<i>p</i> -Toluidine.
<i>p</i> -Bromphenylhydrazine.	<i>m</i> -Toluylenediamine.
<i>p</i> -Chloraniline.	Tribenzylamine.

REAGENTS NOT INCLUDED IN THE PRECEDING GROUPS AND WHOSE
REACTIONS ARE MENTIONED UPON SUCCEEDING PAGES.

<i>m</i> -Chloraniline.	β -Naphthylamine. ¹
Diethylaniline.	Tetrahydroquinoline.
Hexamethylenetetramine.	<i>m</i> -Toluidine.
Monethylamine.	<i>o</i> -Xylidine.
Monomethylaniline.	<i>p</i> -Xylidine.
α -Naphthylamine.	

The bases of the first and second groups were manifestly unsuited for the purpose in mind. Those of the third and fourth groups showing differences in deportment with the several elements under consideration were given more particular attention, while those which were insoluble in dilute alcoholic solutions were placed to one side. The following paragraphs record the observations made with the several bodies which seemed best adapted for quantitative separations.

¹ *Loc. cit.*

Thorium and Zirconium with the Chloranilines.—The different behaviors of the chloranilines substantiate the views held regarding their relative basicity.¹ *o*-Chloraniline did not precipitate thorium or zirconium. *m*-Chloraniline precipitated zirconium in the cold, but with thorium, heat was required to produce precipitation, while *p*-chloraniline precipitated the solutions of both elements, even in the cold. Solutions of cerium, lanthanum, neodymium and praseodymium salts were not affected by these reagents.

Zirconium and Thorium with m-Chloraniline.—Much work was done upon *m*-chloraniline to arrive at the proper conditions in the strength of alcohol and temperature favorable to the complete precipitation of the zirconium solutions, and at the same time to leave the thorium salt unprecipitated. A solution containing equal parts of water and commercial alcohol was found most satisfactory. At a temperature of 60°-70°, this solvent containing *m*-chloraniline occasioned no precipitation in solutions of thorium nitrate, while in zirconium nitrate solutions it precipitated 0.0995 gram, 0.0988 gram, 0.0990 gram and 0.0988 gram of zirconium oxide, instead of 0.0995 gram obtained by ammonia or 0.0993 gram by direct evaporation and ignition. On repeating the experiment with a mixture of the thorium and zirconium nitrates, both elements were completely precipitated.

Thorium and Zirconium with Hexamethylenetetramine (Formin).—Formin in the qualitative tests showed a marked difference in behavior. Thus a thorium solution, after its addition, stood forty-two hours at room temperature without the appearance of a precipitate. Upon adding the zirconium nitrate solution, both hydroxides were precipitated completely.

α - and β -Naphthylamine, *m*-bromaniline and *p*-bromophenylhydrazine precipitated zirconium solutions much more completely than those of thorium, but separations could not be effected by means of them. They reacted indifferently with the salts of cerium, lanthanum, neodymium and praseodymium. *o*-Bromaniline was not tried at all in this investigation.

In a solution of the nitrates of zirconium and cerium, *m*-chloraniline precipitated 0.0532 gram of zirconium oxide, instead of 0.0539 gram obtained with ammonia water. *p*-Chloraniline precipitated 0.0536 gram, *m*-bromaniline 0.0524 gram, and β -naph-

¹ Van't Hoff's "Lectures on Theoretical and Physical Chemistry," Vol. II, p. 102.

thylamine 0.0533 gram. In the first three filtrates 0.0396 gram, 0.0400 gram and 0.0396 gram, respectively, of cerium oxide were obtained, instead of the theoretical 0.0389 gram. In using *p*-chloraniline with a solution containing twice the quantities of zirconium and cerium oxide given above, a very satisfactory quantitative separation resulted.

In precipitating a mixture of zirconium and cerium salts with *p*-toluidine, 0.1341 gram of zirconium oxide was found, while the theoretical amount present was 0.1347 gram. This same reagent added to a solution of thorium and cerium nitrates precipitated 0.1246 gram, 0.1236 gram and 0.1261 gram, instead of 0.1247 gram.

While monomethylaniline precipitated cerium solutions completely and apparently had no marked effect upon those of lanthanum, neodymium and praseodymium, the attempts at quantitative separations were fruitless. Diethylaniline precipitated cerium salts quite completely. The insolubility, however, of this reagent compelled the use of such large amounts of alcohol that serious difficulties arose. These were not overcome. A quantitative separation of cerium from lanthanum was made by means of tetrahydroquinoline. Two precipitations of the cerium were necessary.

o- and *p*-Xylidine, as well as monethylaniline, precipitated cerium completely from its salt solutions. *m*-Toluidine seemed inadequate for this purpose.

p-Toluidine.—From observations made in the qualitative way, it appeared not improbable that *p*-toluidine might be employed to separate zirconium and thorium from lanthanum, neodymium and praseodymium. Accordingly, determinations were made in about 100 cc. of the weak alcoholic solutions, a moderate heat being applied to hasten the reaction. The precipitates formed were quite voluminous and somewhat gelatinous, especially in the case of zirconium, and well adapted for bringing down the accompanying element. On this account one reprecipitation was carried out in each case. The first precipitates dissolved readily in dilute nitric acid, especially if the solutions in the case of zirconium were not allowed to become too warm. The accompanying element was precipitated by ammonia from the combined filtrates. The ignition of the precipitates was conducted with free access of air, in

a porcelain crucible usually, and the blast-lamp used till constant weights were obtained. All of the weights, recorded in grams, are given in the condensed form below. The weights given as "required" were obtained by direct precipitation of the elements, separately, and blasting to constant weight, and represent the average of two closely agreeing results. The "combined" oxides represent the sum of the individual oxides. The results obtained in many cases do not agree well with the standard, but it was thought best to include all which, so far as known, were carried through without accident. Some minor differences in manipulation, such as varying the strength of alcohol, time of digestion, temperature, and volume of solution, were made in different cases. These variations may have influenced the results in some instances.

ZIRCONIUM AND LANTHANUM.

Zirconium oxide.		Lanthanum oxide.		Combined oxides.	
Found.	Required.	Found.	Required.	Found.	Required.
0.1342	0.1341	0.0399	0.0409	0.1741	0.1750
0.1301	0.1341	0.0993	0.1023	0.2294	0.2364
0.1314	0.1341	0.1025	0.1023	0.2339	0.2364
0.1367	0.1341	0.0954	0.1023	0.2321	0.2364

ZIRCONIUM AND NEODYMIUM.

Zirconium oxide.		Neodymium oxide.		Combined oxides.	
Found.	Required.	Found.	Required.	Found.	Required.
0.1349	0.1341	0.0413	0.0457	0.1762	0.1798
0.1439	0.1341	0.0973	0.1142	0.2412	0.2487
0.1372	0.1341	0.1102	0.1142	0.2474	0.2487
0.1446	0.1341	0.0952	0.1142	0.2398	0.2487

ZIRCONIUM AND PRASEODYMIUM.

Zirconium oxide.		Praseodymium oxide.		Combined oxides.	
Found.	Required.	Found.	Required.	Found.	Required.
0.1317	0.1341	0.0420	0.0458	0.1737	0.1799
0.1344	0.1341	0.1099	0.1144	0.2443	0.2485
0.1312	0.1341	0.1129	0.1144	0.2441	0.2485
0.1304	0.1341	0.1014	0.1144	0.2318	0.2485

THORIUM AND LANTHANUM.

Thorium oxide.		Lanthanum oxide.		Combined oxides.	
Found.	Required.	Found.	Required.	Found.	Required.
0.1254	0.1247	0.0407	0.0409	0.1661	0.1656
0.1222	0.1247	not det.	0.1023
0.1246	0.1247	0.1035	0.1023	0.2281	0.2270
0.1243	0.1247	0.1034	0.1023	0.2277	0.2270

THORIUM AND NEODYMIUM.

Thorium oxide.		Neodymium oxide.		Combined oxides.	
Found.	Required.	Found.	Required.	Found.	Required.
0.1254	0.1247	0.0464	0.0457	0.1718	0.1704
0.1232	0.1247	0.1146	0.1142	0.2378	0.2389
0.1242	0.1247	0.1142	0.1142	0.2384	0.2389
0.1242	0.1247	0.1129	0.1142	0.2371	0.2389
0.1248	0.1247	0.1118	0.1142	0.2366	0.2389

THORIUM AND PRASEODYMIUM.

Thorium oxide.		Praseodymium oxide.		Combined oxide.	
Found.	Required.	Found.	Required.	Found.	Required.
0.1253	0.1247	0.0471	0.0458	0.1714	0.1705
0.1214	0.1247	0.1147	0.1144	0.2361	0.2391
0.1238	0.1247	0.1160	0.1144	0.2398	0.2391
0.1246	0.1247	not det.	0.1144

It will be noticed that the results with zirconium are not so satisfactory as those with thorium. This cannot be attributed to any difference in manipulation for they were obtained under similar conditions, the usual practice being to carry on the six separations at one time.

A tendency on the part of zirconium to resist separation from other elements is again indicated here. This tendency is exhibited by its precipitation being retarded by the presence of another element, and by the fact that when once brought down it frequently is contaminated by that element. In the attempts to separate zirconium from thorium by *m*-chloraniline, it was repeatedly noticed that conditions of digestion, sufficient to cause precipitation of zirconium by itself, were inadequate when thorium was present, and when the precipitate was thrown down it was badly contaminated with thorium. Similar observations were made when formin was used to effect their separation; in that case all of the thorium came down with the zirconium under conditions which failed to precipitate thorium when alone. It might be supposed that this peculiar behavior of zirconium would not be noticed upon passing from thorium to the more basic elements, but a number of the results obtained in connection with lanthanum and praseodymium show incomplete precipitations of zirconium, while neodymium was so inclined to come down with zirconium that a satisfactory separation could only be expected when all possible precautions had been taken to prevent it.

The oxides obtained by ammonia from the filtrates weighed less in the separations from zirconium than in those from thorium. If one attempts to attribute this difference to the greater solvent action of the filtrates from the zirconium, the only respect that suggests itself in which the two sets of filtrates differed is that they probably contained different amounts of the precipitant, *p*-toluidine. More of this reagent was necessary to effect a precipitation in the solutions containing thorium than in those in which zirconium was present, and it is probable that in carrying out the two precipitations, as was done in each instance, considerably more *p*-toluidine accumulated in the filtrates from the thorium. Sufficient attention was not given to this point while the determinations were being made to warrant an opinion as to the extent of its influence and it is merely offered as a possible explanation. As both the first and second precipitations were usually made from about 100 cc. of solution, the combined filtrates and washings, in which the precipitations by ammonia were made, were of considerable volume, and the question of the solvent effect of all this solution upon the precipitate produced by ammonia presented itself at the time of the determinations. The final filtrates were usually partially distilled, the bulk of the alcohol and ammonia being obtained in the distillate, from which the alcohol was recovered. More ammonia was repeatedly added to the undistilled portions to see if further precipitation would take place. In a few instances the entire solution was evaporated to dryness and the residue ignited and weighed. The weights obtained substantially made good the discrepancies between the combined oxides "obtained" and "required," but as no blank determinations were made it was not proved that some of this may not have come from extraneous sources.

As previously stated, the recorded results were obtained by the use of the blast-lamp till practically constant weights resulted. The writer is of the opinion, however, that errors may have occurred in this connection due to a constant composition not always being obtained, especially with lanthanum, neodymium and praseodymium. The weights obtained, by blasting the first two, were frequently 10 per cent. lower than those obtained by igniting over a Bunsen burner; there was less difference with praseodymium. Hitchcock¹ found that neodymium and praseodymium sesquioxides, by gentle ignition with free air access,

¹ This Journal, 17, 525.

gradually took on oxygen till the weights approximated those represented by the formula M_2O_7 .

Herzfeld¹ speaks of neodymium oxide as having a blue color and assigns to it the composition Nd_2O_3 , and again,² in an abstract from Shapleigh's investigation, mentions a suboxide as a gray powder and a peroxide as a dirty gray powder. The oxide obtained in the present investigation was invariably of a light brown color resembling cocoa powder, after ignition with the Bunsen burner, and was usually changed to a light blue or light purple color by blasting. It was often necessary to pulverize and blast a long time before the bluish color was uniformly obtained; indeed, in some instances part of the oxide still retained the cocoa color even though by excessive blasting practically no change in weight resulted. In view of the inadequate and somewhat conflicting information concerning neodymium oxides, the composition of the oxide obtained in any particular case must receive careful attention. The change of color produced by blasting the lanthanum and praseodymium oxides was not sufficient to indicate a change in composition, but the weights, especially with lanthanum, were considerably reduced and the certainty of a definite composition should also be established in this instance.

The most that was attempted, during the present work, with any of the oxides, was to compare the weights obtained in the course of the analyses with those obtained by direct precipitation from the aqueous solutions by ammonia, and blasting until they were constant within a few tenths of a milligram. It would seem as though the oxides obtained in this manner would be of constant composition, but it is not improbable that small variations may have occurred and that lack of nice conformity may occasionally be attributed in part to this cause. The mechanical condition of the oxides previous to blasting was not always the same, and it seems not improbable that this fact may be of some importance where intense blasting is resorted to in order to remove the last traces of oxygen necessary to effect a complete transition from an oxide which, for example, is stable at the temperature reached by the Bunsen burner to one of a lower state of oxidation which may be the stable form at the temperature produced by the more intense heat of the blast-lamp. Judging from the experience of Hitch-

¹ *Chemie der seltenen Erden*. p. 63.

² *Ibid.*, p. 122.

cock, and from the fact that blasting invariably reduced the weights, it seems probable that, in the case of some of the elements, at least, an oxide of a higher state of oxidation was more stable over the Bunsen burner than over the blast-lamp. Such behaviors have been noticed with some of the more common elements.

UNIVERSITY OF PENNSYLVANIA.

FLUORIDE OF GOLD.¹

By VICTOR LENHER.

Received September 8, 1903.

INASMUCH as flucrspar is frequently associated with gold in nature, and quite notably so in the deposits of the telluride ores, it has seemed important to study gold fluoride in order to determine, if possible, whether this substance can play any part in the genesis of these deposits.

The known compounds of gold with the halogens chlorine, bromine and iodine, are, as a rule, fairly well defined. In the trivalent condition, gold forms the relatively stable chloride while the bromide and iodide show greater tendency to break down into the lower state of valence of gold.

The halides in which gold shows a monovalence have received considerable attention, and it is known with a reasonable degree of certainty under what conditions aurous chloride, bromide, and iodide are capable of existence.

While the chlorides, bromides and iodides of gold have received more or less study, comparatively little is known of fluoride of gold. Prat² has prepared an intermediate oxide of gold, Au_2O_3 , by the incomplete solution of gold in aqua regia, in which the hydrochloric acid is in excess, treating the solution with sufficient potassium bicarbonate to dissolve the precipitate formed, and warming the clear orange-yellow solution to 95° , when a dark olive-green precipitate was obtained which, when dried, showed the composition Au_2O_3 . In studying the properties of this oxide, Prat states that hydrofluoric acid combines with it but without dissolving it. In his study of the action of fluorine on the various metals, Moissan states that at a red heat, gold is attacked by

¹ Read before the Wisconsin Academy of Science, December 26, 1902, and published in the Transactions.

² *Compt. rend.*, 70, 843.

fluorine gas, a yellow hygroscopic substance being formed, and that this substance is readily decomposed into gold and fluorine.

These two experiments give practically what is known of the fluoride of gold.

The activity of the halogens toward other elements is, as a rule, inversely proportional to their atomic weights. The first member of this group of active elements, fluorine, is certainly the most active of all the elements, be they halogens or not; yet, as will be demonstrated later, it appears to have little if any affinity for gold.

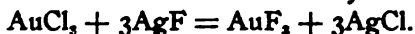
In studying the chemistry of gold, it should always be borne in mind that it is the most inactive of the metals, but the relative stability of the most of its salts, notably with the halogens, would appear to make probable the relative stability of the compound of the most active of the elements, fluorine. On the other hand, we have the marked difference of fluorine from the other halogens in the insoluble fluorides of calcium, strontium and barium, as contrasted with the very soluble chlorides, bromides and iodides; and the soluble fluorides of silver and thallium as compared with the insoluble chlorides, bromides and iodides.

In order to study the relations between fluorine and gold, experiments were conducted with the view of bringing about, if possible, the formation of gold fluoride under various possible conditions.

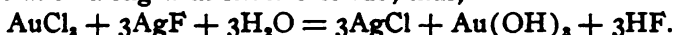
The first experiment made was a study of the action of hydrofluoric acid on gold oxide. To this end, gold oxide was prepared by the action of magnesium oxide on a solution of gold chloride and the excess of magnesia removed with nitric acid. The gold oxide thus obtained was finely divided, and hence in the most suitable condition to be susceptible to any chemical action. This gold oxide can remain in contact with hydrofluoric acid indefinitely or, as has been the case, can be boiled for weeks with either hydrofluoric acid alone or with a mixture of hydrofluoric and nitric acids, without suffering any change whatever. These experiments have been repeated several times, but in no case has gold been found to enter into solution, nor has it been possible to detect fluorine in the precipitate. It is obvious that gold fluoride cannot be prepared by the action of hydrofluoric acid on the oxide. The next most natural method to try

for the preparation of the fluoride would be that of double decomposition.

Silver fluoride and gold chloride, both being soluble salts, on being brought in contact in solution should yield theoretically:



The actual case is that when solutions of these two salts are brought in contact, gold hydroxide is quantitatively thrown out of solution along with silver chloride; thus,



The accuracy of this reaction has been carefully established in the laboratory.

If gold fluoride is even momentarily formed, it is immediately decomposed by water.

The method yet remaining for the preparation of a substance incapable of existence in presence of water would be the use of anhydrous solvents. A large number of organic solvents have been tried with this end in view, but no substance has been found which would dissolve both gold chloride and silver fluoride; either these salts are insoluble or are decomposed by the substances worked with. Among the solvents examined, mention may be made of the following: Alcohol, ether, carbon bisulphide, benzene, turpentine, pentane, hexane, chloroform, carbon tetrachloride, ethyl nitrate, nitrobenzene, ethyl acetate, ethyl propionate, and pyridine.

It thus appears that gold fluoride is incapable of existence not only in presence of water, but under the ordinary conditions met with in the laboratory and in nature.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI, No. 60.]

A METHOD FOR THE ESTIMATION OF CHLORIDES, BROMIDES AND IODIDES.

BY STANLEY BENEDICT AND J. F. SNELL.

Received September 3, 1903.

IN THE August number of this Journal we described a method for the detection of chlorides, bromides and iodides in presence of each other. The reagent used to liberate the iodine and bromine was potassium iodate, which sets free the iodine on acidifi-

cation with acetic and the bromine on acidification with dilute nitric acid. In the same paper we mentioned that the reaction with iodic acid had been employed by Bugarszky¹ for the quantitative separation of chlorides and bromides. He liberated the bromine with potassium biiodate and dilute sulphuric acid, and determined (1) the excess of biiodate and (2) the chlorine. This method is evidently inapplicable in presence of iodides. The purpose of the present paper is to describe a method of estimation of all three halogens when present together. It includes determinations of (1) total halogens, (2) iodine, and (3) chlorine, the bromine being estimated by difference.

The total halogens are determined by any of the ordinary methods, gravimetric or volumetric.

For the determination of the iodine, a suitable quantity of the substance (containing not over 0.5 gram iodine or 0.15 gram chlorine, if tenth-normal solutions are to be used) is dissolved in water and made up to about 50 cc. in a 100 cc. glass cylinder with close-fitting glass stopper. Neutral potassium iodate is added in about twice the quantity necessary to react with all the bromine and iodine believed to be present. The mixed solution is acidified with 4 or 5 cc. 5N (30 per cent.) acetic acid and shaken with 30-40 cc. carbon disulphide until all the liberated iodine has been taken up by the latter. The aqueous phase is now separated from the carbon disulphide phase by filtration through a wet filter, and the carbon disulphide is thoroughly washed with cold water on the filter. The filtrate and washings are reserved for the chlorine determination. The carbon disulphide solution is transferred to another beaker by puncturing the filter and is covered with 20-25 cc. 75 per cent. alcohol. Any carbon disulphide left adhering to the filter is rinsed down into the beaker with a portion of the 75 per cent. alcohol. The iodine is now titrated with sodium thiosulphate with constant stirring. No starch indicator is necessary.

For the determination of the chlorine, the aqueous filtrate from the carbon disulphide is treated with 5 cc. 5N nitric acid (sp. gr. 1.18) to liberate the bromine and is boiled in a covered beaker until colorless. The excess of iodate is next destroyed by adding a quantity of potassium iodide slightly in excess of the amount necessary to react with it. The solution is again boiled until colorless, 2 or 3 cc.

¹ *Ztschr. anorg. Chem.*, 10, 387 (1895).

TABLE OF RESULTS.

	KL. Grams.	KBr. Grams.	NaCl. Grams.	KL. Grams.	KBr. Grams.	NaCl. Grams.	KL. Grams.	KBr. Grams.	NaCl. Grams.
Used.....	0.0798	0.0897	0.0893	0.0114	0.0640	0.0638	0.1140	0.1281	0.1277
Found.....	0.0796	(0.0896)	0.0896	0.0116	(0.0640)	0.0636	0.1138	(0.1285)	0.1275
Difference.....	-0.0002	+0.0003	+0.0002	-0.0002	-0.0002	-0.0002
" per cent.	-0.25	+0.34	+1.75	-0.31	-0.18	-0.16
Used.....	0.0456	0.0512	0.0510	0.1026	0.1152	0.1143	0.0228	0.2140	0.0255
Found.....	0.0457	(0.0511)	0.0510	0.1025	(0.1152)	0.1144	0.0230	(0.2141)	0.0252
Difference.....	+0.0001	0.0000	-0.0001	+0.0001	+0.0002	-0.0003
" per cent.	+0.22	0.00	-0.10	+0.09	+0.09	-0.12
Used.....	0.1710	0.0512	0.0127	0.0114	0.0128	0.0128	0.0114	0.0128	0.0127
Found.....	0.1704	(0.0507)	0.0128	0.0105	(0.0134)	0.0131	0.0116	(0.0125)	0.0128
Difference.....	-0.0006	+0.0001	-0.0009	+0.0003	+0.0002	+0.0001
" per cent.	-0.35	+0.79	-7.89	+2.34	+1.75	+0.80
Used.....	0.0057	0.0064	0.0635	0.1368	0.0064	0.0063	0.1228	0.3815	0.1518
Found.....	0.0060	(0.0062)	0.0634	0.1369	(0.0066)	0.0060	0.1225	(0.3816)	0.1520
Difference.....	+0.0003	-0.0001	+0.0001	-0.0003	-0.0003	+0.0002
" per cent.	+5.26	-0.16	+0.07	-4.76	-0.25	+0.13

more of the dilute nitric acid being added, if the color is not completely discharged after ten or fifteen minutes' boiling. A minute or two after the color has completely disappeared the solution is taken from the flame, cooled and neutralized with sodium carbonate. To secure exact neutralization, a little calcium carbonate may be added at first and then sodium carbonate solution until a precipitate just forms. The chlorine is then determined by titration with standard silver nitrate, using potassium chromate as indicator.

The results of twelve analyses of mixtures of potassium iodide, potassium bromide and sodium chloride are tabulated below. It will be observed that, with two exceptions, the differences between the taken and found quantities of potassium iodide and sodium chloride do not exceed 0.3 milligram.

ON CEROPTENE, A NEW ORGANIC COMPOUND.

BY W. C. BLASDALE.

Received August 21, 1903.

IN AN article published¹ in 1893 the writer briefly described an organic compound which had been obtained from the fronds of *Gymnogramme triangularis*, for which the name *ceroptene* was provisionally proposed. It was shown in that paper that this compound, together with others of unknown composition, was secreted by peculiar gland-tipped hairs, which were found in great abundance on the under surfaces of the fronds of the before-mentioned plant. The yellow secretion is produced in such abundance as to completely envelop and conceal the dorsal surfaces of the fully developed fronds, whence the popular name of the plant, the "golden-back" fern.

Secretions of a somewhat similar character are produced by other species of ferns, especially certain groups of species belonging to the genera *Gymnogramme*, *Cheilanthes* and *Notholaena*; possibly, also the secretions produced by certain species of *Primula* are of a like nature. Though none of these secretions appear to have been submitted to a chemical investigation, the opinion expressed or implied in most of the botanical treatises, which deal with these plants is that they consist of wax. Goep-

¹ *Erythraea* (botanical journal published at Berkeley from 1893 to 1899), 1, 252.

pert,¹ however, considered them to be of a resinous nature, though his only reason for doing so is their solubility in alcohol. Klotzsch² has also described a crystalline compound which he obtained accidentally by dissolving the indument from the fronds of various species of *Gymnogramme* with alcohol and allowing the solution to evaporate spontaneously. This substance melted at 50°, was soluble in hot water, and in the opinion of this investigator was a "pseudo-stearoptene," that is, a compound related to coumarine, an opinion for which very little evidence was offered.

Though the golden-back fern is a comparatively common species on the Pacific coast, the amount of secretion yielded by it is but small, and it has been a difficult matter to secure the large quantities necessary for the investigation. The work has been further hindered because many of the compounds obtained were of a tarry nature and could not be purified when working on the small amounts available. Inasmuch as a large number of facts regarding the properties of the compound ceroptene have been gradually acquired it has seemed advisable to publish these at the present time, even though final conclusions regarding its structural formula can not be offered.

PREPARATION OF CEROPTENE.

Experiments with a variety of solvents showed that the entire secretion is easily soluble in either benzene or petroleum-ether, more readily, however, in the former solvent. The dried fronds, exclusive of stems, were treated in an extraction apparatus with either one of these solvents till complete solution of the indument had been effected, the solution thus obtained filtered from spores, etc., the excess of solvent distilled off, and the residual solution allowed to evaporate. In time there appeared wart-like groups of platy crystals, together with a much larger amount of a yellow amorphous substance, the total yield ranging from 4.4 to 6.4 per cent. Repeated crystallization of the crystalline portion from either benzene, ethyl ether, or alcohol finally gave a compound which melted very sharply at 135°. This is the compound to which the name ceroptene has been given; it constitutes about one-third of the total secretion. The non-crystalline portion melts

¹ "*Actorum Academiae Caesaræ Leopoldino-Carolinæ Naturæ Curiosorum*," 18, Suppl. I, page 229.

² *J. prakt. Chem.*, 55, 242

at about 58° and is evidently a mixture of several substances, of which the only one identified with certainty is cerotic acid. Various methods of treating this portion were used; the most satisfactory was to digest with a dilute aqueous solution of potassium hydroxide, in which the cerotic acid is but slowly soluble, while the other constituents of the secretion dissolve almost immediately. The insoluble cerotic acid was purified by repeated treatment with hot alcohol. The alkaline solution was acidified, which reprecipitated the tarry substance held in solution, and the precipitate thus produced treated with a small amount of cold alcohol. This treatment left insoluble a further quantity of ceroptene and a very minute quantity of a second crystalline substance. Thus far but little progress has been made in the separation of the tarry products dissolved by the alcohol.

DESCRIPTION OF CEROPTENE.

The pure substance forms beautiful tabular or prismatic crystals of a sulphur-yellow color. It is readily dissolved by acetone, chloroform, carbon bisulphide, carbon tetrachloride, and less readily by ether. It is readily soluble in alcohol or benzene, but the solubility is greatly increased by a slight increase in the temperature of these solvents. Concentrated sulphuric, hydrochloric, or acetic acids readily dissolve ceroptene and it may be recovered from the two latter solvents by spontaneous evaporation. Dilution of all of the three acid solutions produces a light yellow precipitate, which on treatment with benzene yields the original ceroptene. With the sulphuric acid solution, however, the precipitation takes place very slowly and small amounts of tarry substances are produced at the same time. On heating, it fuses with the formation of a clear lemon-yellow liquid but, as the temperature is increased, decomposes with the formation of volatile compounds, which have a strong aromatic odor. By transmitted light, the crystals are of a clear lemon-yellow color, but by reflected light they show a pronounced green fluorescence. The alcoholic solution also shows the latter phenomena to a slight degree. Neither the crystals nor their solutions rotate the plane of polarized light. The specific gravity of the crystals at a temperature of 15° , compared with water at the same temperature, is 1.1976.

CRYSTALLOGRAPHY OF CEROPTENE.

Crystallization from different solvents produced individuals showing a considerable diversity of habit, though the number of distinct crystal forms concerned was not great. The best were obtained from benzene, from which solvent perfect individuals of flat, tabular form sometimes 2 cm. in length and 3 mm. in thickness could be obtained; chloroform or glacial acetic acid gave less perfect forms; alcohol usually gave needle-shaped or prismatic forms of smaller size. Examination of the crystals with polarized light in a direction at right angle to the plane of greatest development showed the emergence of an optic axis, the latter placed very eccentrically. This fact, as well as the symmetry of the crystal form, clearly classes them as triclinic. The plane of greatest development was, therefore, chosen as the base and the two planes showing the least inclination to it, as brachy- and macropinacoids; it was then easy to refer the remaining planes to either dome or prismatic faces. Although the crystals were well formed, many of the faces, especially the macropinacoid, failed to give good reflections owing to the curvatures or other imperfections. The accompanying table gives the results of the measurements of the principal interfacial angles.

MEASUREMENTS IN THE BRACHY ZONE.

Angle $(001) \wedge (010)$. Average of seven measurements, $67^{\circ} 29'$.

Angle $(0\bar{1}0) \wedge (0\bar{1}1)$. Average of two measurements, $55^{\circ} 59'$.

Angle $(001) \wedge (0\bar{1}1)$. Average of three measurements, $56^{\circ} 57'$.

Angle $(001) \wedge (011)$. Result of one measurement, $33^{\circ} 39'$.

MEASUREMENTS IN THE MACRO ZONE.

Angle $(001) \wedge (100)$. Average of four measurements, $85^{\circ} 45'$.

Angle $(\bar{1}00) \wedge (\bar{1}01)$. Average of two measurements, $42^{\circ} 52'$.

Angle $(001) \wedge (\bar{1}01)$. Average of eight measurements, $50^{\circ} 49'$.

MEASUREMENTS IN THE VERTICAL ZONE.

Angle $(100) \wedge (010)$. Average of five measurements, $84^{\circ} 11'$.

Angle $(0\bar{1}0) \wedge (\bar{1}20)$. Average of five measurements, $30^{\circ} 24'$.

Angle $(100) \wedge (\bar{1}20)$. Average of three measurements, $66^{\circ} 10'$.

From the figures representing the inclinations of the three pinacoids, the following values were calculated¹ for the inclinations of the axes:

¹ The writer desires to acknowledge his indebtedness to Dr. A. S. Eskle, of the Department of Mineralogy, for assistance in making the calculations.

$$\alpha = 112^{\circ} 13', \beta = 92^{\circ} 12', \gamma = 94^{\circ} 33'.$$

From the inclinations of the two dome faces (d and e of the figures) on the base, the following values for the axial ratios were obtained:

$$a = 0.8353, b = 1, c = 1.0138.$$

From the intersection of the face m on the brachy- and macro-pinacoids, the intersection of that plane on the a and b axes respectively, was found to be 1.757; 1, hence its formula is (120) . It was observed only when truncating the more acute of the two prismatic angles formed by the intersection of the macro- and brachy-diagonal sections. The macrodome face was present only when of the form $(10\bar{1})$. The brachydome face of the form $(0\bar{1}1)$ was the one usually present, though the form (011) was observed in two instances. Some of the more common combinations are shown in the accompanying figures in which $a = (100)$, $b = (010)$, $c = (001)$, $d = (01\bar{1})$, $e = (10\bar{1})$, $f = (011)$, $m = (\bar{1}20)$.

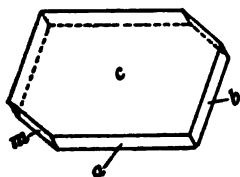


Fig. 1.

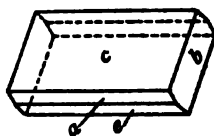


Fig. 2.

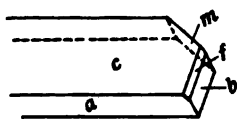


Fig. 3.

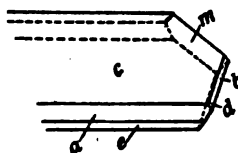


Fig. 4.

FORMULA OF CEROPTENE.

In order to obtain satisfactory material for the quantitative examination, very careful preparation was found to be necessary, since the crystals tend to retain very tenaciously small amounts of the waxy constituents of the secretion. Failure to discover this fact led to an erroneous determination of the formula in the

first work on the subject. Of the results recorded below, No. 1 represents materials recrystallized three times from ether, after the preliminary purification, Nos. 2 and 3 were obtained similarly by three recrystallizations from benzene and Nos. 4 and 5 by three recrystallizations from absolute alcohol.

	(1)	(2)	(3)	(4)	(5)	Average.
Carbon.....	72.26	72.42	72.62	72.62	72.51	72.48
Hydrogen.....	6.37	6.16	6.13	6.16	6.20	6.20

These figures indicate that the formula of the compound is $(C_9H_8O_2)_n$, the theory for which is $C = 72.44$, $H = 6.09$.

The molecular weight was determined by the freezing-point method, using the usual form of Beckmann apparatus. The results obtained were: With benzene as a solvent, 253, 264, 255; with glacial acetic acid as a solvent, 268, 280; with phenol as a solvent, 259.

The correct formula of the compound then must be $C_{18}H_{16}O_4$ (molecular weight = 298), the low results obtained being probably due to a slight amount of dissociation.

REACTIONS OF CEROPTENE.

The compound possesses decided acid properties. It is dissolved readily by even dilute solutions of the alkaline hydroxides, and these solutions remove it rapidly from a benzene solution of the compound. Long-continued treatment with hot solutions of sodium or barium carbonate or borax dissolve it to some extent. In spite of these facts, it is a difficult matter to prepare the pure salts, owing to their unstability.

If a solution of ceroptene in an alkaline hydroxide is gradually concentrated, oily, yellowish-brown drops finally appear in the bottom of the vessel; these solidify, on cooling, with the formation of a hard, yellow mass, which is easily soluble in water. If some of this solid yellow mass is dissolved and the solution thus obtained is allowed to evaporate spontaneously, the ceroptene gradually separates out in the form of granular masses and the residual solution becomes alkaline. Dilution of alkaline solutions of ceroptene does not bring about precipitation, but neutralization results in the formation of a light yellow precipitate, and, when this is dissolved in benzene, ceroptene crystals of the usual form are produced on evaporation. All

the alkaline solutions possess a much more intense color than solutions of the corresponding concentration in organic solvents. Two samples of the potassium salt, prepared with the use of the smallest possible excess of the alkali and separated as solid yellow masses, gave 11.94 and 11.42 per cent. of potassium, respectively. A salt corresponding to the composition $C_{18}H_{17}KO_4$ should contain 11.64 per cent.

The barium salt was prepared by boiling ceroptene with a slight excess of barium hydroxide, filtering the hot solution into a flask previously filled with hydrogen, and allowing to stand. After several days, there appeared a beautifully crystalline salt of a deep yellow color. It is but slightly soluble in water and, on heating, decomposes before reaching a definite melting-point. Determination of the per cent. of barium in two preparations of the salt gave 17.92 and 17.79 per cent., respectively. These figures would indicate a compound corresponding to the formula $(C_{18}H_{17}O_4)_2Ba \cdot 2H_2O$, which should contain 17.87 per cent. of barium and 4.69 per cent. of water of crystallization. Experiments in heating the salt showed no appreciable loss up to a temperature of 120° , but at 160° the salt lost 5.23 per cent. in weight and there was some evidence of decomposition.

The silver and lead salts may be obtained by the addition of the nitrates of these metals to solutions of the potassium salt. As thus obtained, they consist of gray, amorphous precipitates which are difficultly soluble. Determination of the silver in a sample of this salt (probably contaminated with small amounts of silver oxide) gave 27.62 per cent. of silver, whereas the anhydrous salt should contain 26.66 per cent.

Attempts to acetylate ceroptene, using glacial acetic acid as a solvent and various combinations of acetic anhydride, acetyl chloride and sodium acetate were entirely unsuccessful. Either the original compound was obtained unchanged, or tarry decomposition products only were produced. Similarly, treatment with benzoyl chloride failed to give any evidence of a definite reaction. With bromine in a chloroform solution, ceroptene liberates at once hydrobromic acid, but the other products of the reaction are non-crystalline and could not be purified. With "Hübl's mixture," using the usual method for the determination of the iodine absorption, no absorption of iodine was shown.

Phenylhydrazine and hydroxylamine do not react with ceroptene under the conditions which usually bring about reactions with aldehydes or ketones, and no bisulphite compound could be prepared. No indications of reducing properties could be obtained by the use of the usual reagents, *i. e.*, alcoholic silver nitrate, Fehling's solution, etc.

Oxidizing agents, dilute nitric acid or potassium permanganate or bichromate in alkaline solution, added to ceroptene and heated, at once give a pronounced odor of benzaldehyde. When 0.5 gram of ceroptene was heated with potassium permanganate for an hour, filtered from the precipitate of manganese dioxide which is formed, acidified and extracted with ether, a white crystalline compound was obtained. This, after purification by recrystallization, was found to melt at 122° , and was sublimed without change. When it was dissolved in absolute alcohol, the solution saturated with dry hydrochloric acid gas, and the whole poured into cold water, oily drops having the characteristic odor of ethyl benzoate separated out. Some carbon dioxide is produced during the oxidation, but it is evident that the chief product of the reaction is benzoic acid, though it is probable that the corresponding aldehyde is first produced.

The treatment of a glacial acetic acid solution of ceroptene with concentrated aqueous hydriodic acid at a temperature of 60° or above, produces a crystalline iodo-compound, which melts at 182° . This appears in crystalline form on cooling the hot mixture, and continues to separate from the solution during several days. The yield obtained in six different preparations ranged from 131 to 145 per cent. of the ceroptene used. Many attempts were made to separate other products of the reaction from the acid mixture, but in every case only tarry compounds, which in solubility, etc., seemed to be identical with the crystalline iodo-compound, were obtained. Iodine is not liberated during the reaction, nor was any considerable amount of the free iodine, which was present in the hydriodic acid used, taken up. The reaction does not take place when other solvents are substituted for the acetic acid, nor does an analogous reaction take place when hydrochloric or hydrobromic acids are used in place of hydriodic acid.

THE IODO-COMPOUND.

The crystals are needle-shaped, often an inch long, with blunt terminations, but the faces are too imperfect to admit of crystallographic study. By transmitted light they are red-brown, but by reflected light they are dark purple. On heating, they first melt with the liberation of iodine, then carbonize, and finally burn without residue. They are insoluble in water, carbon bisulphide and petroleum ether, only slightly soluble in glacial acetic acid, benzene and nitrobenzene, but readily so in alcohol and acetone. It is, however, almost impossible to recrystallize the compound from any of these solvents; when dissolved in alcohol or acetone, the solution leaves, on evaporation, a black, tarry mass which seems to possess all the chemical properties of the original crystals. If acetic acid is added to the acetone solution, a very small amount of the compound separates in crystalline form, the remainder as an amorphous mass. The composition of the compound is shown in the following analyses, each of which represents a different preparation, obtained by washing the crystals, which separated out with glacial acetic acid, and drying at 110° . The iodine was determined by the Carius method, but most of the determinations are somewhat high, owing to the presence of minute particles of glass which could not be separated from the precipitate.

	(1)	(2)	(3)	(4)	(5)	Average.
Carbon.....	41.26	41.20	41.34	41.07	41.22	41.22
Hydrogen	3.44	3.43	3.44	3.41	3.43
Iodine	40.25	40.84	40.69	40.59

These figures correspond most nearly to the composition $C_{11}H_{11}IO_3$, the theory for which is $C = 41.51$, $H = 3.46$, $I = 39.94$.

The molecular weight was determined with approximate accuracy only; the small amount of material available necessitated the use of freezing-point methods and the very slight solubility, in the solvents commonly employed, introduced a large percentage error in these determinations. Using nitrobenzene as a solvent, two approximate results, 310 and 357 respectively, were obtained. The theory for $C_{11}H_{11}IO_3$ is 318. These results are sufficient to establish the formula of the compound as written above.

REACTIONS OF THE IODO-COMPOUND.

The iodo-compound shows acid properties similar to those of ceroptene, but the preparation of the pure salts is attended with many difficulties. The salts are characterized by red or brown colors and possess weak dyeing properties with woolen goods. An approximately pure potassium salt yielded 15.27 per cent. of potassium; the compound $C_{11}H_{11}KO_4$ should contain 15.89 per cent. If an alkaline solution of the iodo-compound is acidified, there is produced a yellow precipitate which coagulates to form resinous masses. It is soluble in alcohol, acetone, chloroform and glacial acetic acid, but it can not be crystallized from any of these solvents or combinations of them. It does not contain iodine and melts very indefinitely at 52° . Owing to its amorphous nature and the difficulty of drying without effecting decomposition, an accurate determination of its formula could not be made. The result of three combustions and a single molecular weight determination indicate that the formula is $C_{11}H_{12}O_4$.

On oxidizing the iodo-compound with nitric acid or potassium permanganate, as in the treatment of ceroptene, similar evidence for the formation of benzaldehyde and benzoic and carbonic acids was obtained. With the usual reagents for the detection of aldehyde or ketone groups, no evidence of any reaction could be obtained. Attempts to reduce with sodium amalgam and also with metallic magnesium led to the formation of compounds which could not be purified.

The exact nature of the reaction involved in the formation of the iodo-compound is still a mystery. Apparently, it is the only product of that reaction. If it be assumed that 1 molecule of ceroptene produces 1 molecule of the iodo-compound, the theoretical yield should be 106.7 per cent. Since the actual yield varies from 131 to 145 per cent. and since a large amount of a non-crystalline compound, which seems to be identical with the crystalline product, is produced at the same time, it is probable that 2 molecules of the iodo-compound are produced from 1 of ceroptene. Evidently the acetic acid takes part in the reaction, as is also evinced by the failure to obtain the compound when other solvents are used. Further, this involves more than the simple addition of an acetyl group, since no evidence of acetic

acid nor of any volatile compound could be obtained on saponifying, acidifying the product, and distilling. As to the structure of the iodo-compound, it can only be said at present that it contains a single benzene nucleus with a side chain, and that, since the iodine is easily displaced, it is not a part of a second ring, though as the substance does not add iodine, and hence contains no ethylene groupings, it is somewhat difficult to write a structural formula in which the ring structure is absent. At first sight it would seem as though the quantitative relation involved in the formation of the iodo-compound would indicate that ceroptene was composed of two symmetrical groups, each containing a single benzene nucleus, which is split by the hydriodic acid. If this were strictly so, however, the formation of dibasic as well as monobasic salts should be expected. Any attempt to express the probable structure of either compound is at present unprofitable.

IDENTIFICATION OF CEROTIC ACID.

If the waxy portion of the secretion, which remains after the separation of the ceroptene, is digested with hot alcohol, filtered while hot, and allowed to cool, a white amorphous precipitate separates out. This precipitate fused at 64° and, on cooling, formed a hard, brittle mass. By two further precipitations from alcohol, a product was obtained which melted at 70° . A more rapid method of separating the same substance was to digest the wax with a dilute solution of an alkaline hydroxide and treat the undissolved portion with alcohol as in the other method. When obtained by either process, the product was of a greenish color after fusion, was readily soluble in petroleum ether, acetone and ethyl ether, and was precipitated from the solution by lead acetate. The alcoholic solution shows only faint acid properties, and the amount of potassium hydroxide necessary to react with 1 gram, determined by the ordinary process for saponification number, was found to be 0.22 gram. The combustion of three different preparations gave the following results:

	(1)	(2)	(3)	Theory for $C_{27}H_{44}O_2$
Carbon	79.04	78.29	80.24	78.94
Hydrogen	12.32	12.56	13.30	13.26

A single determination of the molecular weight by the freezing-point method, using benzene as the solvent, gave 482, though the percentage error involved in this determination is comparatively

large, owing to the very slight solubility in this solvent. In all the particulars noted above, the substance agrees so closely with the substance originally separated by Brodie from beeswax that there can be little doubt that it is essentially cerotic acid. The preparations thus far obtained are impure.

THE OTHER CONSTITUENTS OF THE SECRETION.

As noted earlier in this paper, a second crystalline compound is obtained from the tarry precipitate produced by acidifying the alkaline solution of the secretion. Treatment of this precipitate with alcohol leaves a small amount of ceroptene, together with the substance just referred to. It is a difficult matter to separate it from the ceroptene, but a long series of fractional crystallizations from acetone finally separated it in pure condition. It forms brown, monoclinic prisms which melt at 185° . Some of these were obtained large enough for crystallographic study. The only forms present were the prism, basal plane and clinopinacoid. The angles measured were as follows:

$$\begin{array}{lll} (110) > (\bar{1}\bar{1}0) \text{ (average of 9 measurements)} & = 77^{\circ} 32' \\ (110) > (001) \text{ " " 4 " " } & = 57^{\circ} 31' \\ (010) > (001) \text{ (result of a single measurement)} & = 89^{\circ} 34'. \end{array}$$

Barely enough of the pure substance was obtained for a single combustion, the results of which were $C = 69.01$ per cent., $H = 4.95$ per cent.

That portion of the acid precipitate which is easily soluble in cold alcohol, and which forms nearly one-half the total secretion, is of an entirely amorphous nature. In a long series of experiments with a great variety of solvents, only brown, sticky compounds were obtained. The compounds of which this material is composed are evidently strongly acid in character, and their lead salts are insoluble. Combustions of several samples of the substance gave results varying from 57.76 to 68.33 per cent. of carbon, and from 7 to 7.17 per cent. of hydrogen. The material is clearly a mixture of several acids.

THE HYDROCARBONS IN LOUISIANA PETROLEUM.

BY CHARLES E. COATES AND ALFRED BEST.

Received September 1, 1903.

THE excitement which followed the discovery of the Beaumont oil field in Texas and the speculation which attended its development, have, to some extent, drawn the attention of the public from the development of the petroleum fields of Louisiana. Of these, the fields at Welsh and at Jennings have already passed into a solidly commercial condition, while at Anse la Butte, and at numerous other points in Southern Louisiana, oil has been found in considerable quantity. It is the intention of the writer to publish later an account of the chemical nature of the various oil pools in Louisiana. In view of the fact, however, that very little information is available in regard to this matter, it has been considered advisable to present here the results of some work done in this laboratory during the past six months. Early in the spring, samples of oil were secured from Beaumont, Texas, and from the oil fields near Welsh, Jennings, and Breaux Bridge in Louisiana. These oils were distilled from Engler flasks with the usual precautions. Their fuel values were determined with a Parr calorimeter, which gave concordant results on duplicate determinations and proved in every way satisfactory.

In the distillations, it was found that the time taken influenced the results to such an extent that no measurements were concordant above 300°. This is, doubtless, due to the decomposition of the higher fractions, these breaking down slowly into fractions both of lower boiling-point and of higher boiling-point than the original fraction.

The following table shows the results of these examinations:

In the table the distillations were made in duplicate and agreed fairly well. The relative evolution of hydrogen sulphide, at low temperatures, is worth consideration, both from the standpoint of pumping the crude oil and of refining it. The figures obtained for the Beaumont oil differ somewhat from those previously published. It would seem that it had gotten heavier than it was when the Lucas well was first opened, and it also shows a general rise in the boiling-points of the fractions. There are now no gushing wells at Beaumont, and many which once pro-

	Texas. Beaumont.	I.A. Welsh.	I.A. Jennings.	I.A. Breux Bridge.
Specific gravity 25° C.	0.9228	0.9276	0.9093	0.9392
Distillation begins	150° C.	230° C.	200° C.	240° C.
Distillation, Engler flasks, 760 mm.	per cent.	per cent.	per cent.	per cent.
To 150° C.	none	none	none	none
150°-200°	2	none	none	none
200°-250°	8	2	13	1
250°-300°	26	17	28	15
300°-350°	26	23	24	22
350°-to asphalt	30	49	30	53
Asphalt residue	8	9	5	9
H ₂ S evolved on heating	{ in large quantities 115°-150°	in very small amount at 230°	in small quanti- ties 200°	in very small amount at 240°
Color of lower fractions	{ yellow	nearly colorless, light yellow on standing	colorless, yellowish on standing	slightly yellow
Fuel value in B. T. U.	19923	19000	19814	19300
Illuminating oil fractions to 300°	36	19	41	16
Estimated depth of well	1200	700 (?)	1000	600
Per cent. sulphur in crude oil	1.96	0.32	0.39	0.20

duced oil on pumping, have been abandoned. The field at Jennings is of greater area, and less initial pressure. The proved field there is growing and the wells, while not phenomenal, are considered profitable. There is, as yet, no reason to fear that the field is losing in producing power. This is also true of the Welsh field. The geology of these oil deposits is still somewhat obscure. It has been suggested that they are pools, gathered under pressure in the top of a dome with sharply descending sides. Such a deposit would possibly be larger when the angle of the dome was more obtuse. There are, throughout Southern Louisiana, certain elevations of an otherwise flat country. They are generally of limited area and rise only a very few feet above the surrounding plain. These elevations are considered superficial indications of gas pressure beneath and, consequently, of oil. There is also a certain amount of seepage, and some springs show oil in their water. None of these indications are reliable as establishing the existence of an oil pool, which fact, however, would seem to make it probable that many such pools may still remain undiscovered.

In the following investigation the sample sent from Breaux Bridge was taken, first, because it was sent in considerable quantity. The methods employed were those suggested by Mabery in his recent investigations of the Texas oils, and by Richardson and Wallace in their paper on the Beaumont field. A similar treatment of Jennings and Welsh fields will follow as soon as time permits.

The oil in question was sent by the Moresi Co., of Jeanerette, La. It was taken from a 600-foot stratum at Anse la Butte, near Breaux Bridge, La. This is considered a shallow well. There are others at Anse la Butte which are 1000 feet deep and produce 15 to 30 barrels daily. The crude oil was low in sulphur, an analysis, by the Carius method, showing only 0.2 per cent. It was black, viscous and had a not unpleasant odor, somewhat resembling turpentine. The specific gravity, at 25°, was 0.9392. Distilled in an Engler flask, at atmospheric pressure, it gave no gasoline and 16 per cent. illuminating oil—the fractions up to 300° C. Heated to 350° C., 22 per cent. more oil was obtained. Heated above this to asphalt, the distillate was a dark, heavy, fluorescent oil with a somewhat unpleasant odor. After the

limit of the thermometer employed, 400° , was reached, it was removed and distillation continued until little more oil came over. The residue, amounting to about 9 per cent., was heated in an open dish until it was about one-fourth evaporated. The resulting mass was asphaltic in its nature, being hard, black and shiny, with a conchoidal fracture. It had a specific gravity of 1.123. On burning in a closed platinum crucible, as in coal analysis, the following results were obtained:

Volatile matter	71.0
Fixed carbon	28.6
Ash	0.4

Compared roughly with paving asphalt, the physical qualities of this residue appeared only fair.

An attempt was made to refine the illuminating oil fraction by sulphuric acid, in the usual way, washing with sodium hydroxide. It was found practically impossible to secure a water-white product. The most nearly colorless products obtained turned yellow in a few days, on standing in an open Erlenmeyer flask. About 15 per cent. of sulphuric acid was used, and there was a loss of about 12 per cent. of oil, though these figures could probably be reduced in practice. The refined oil was tested in an ordinary flat-wick lamp. It burned freely with a somewhat smoky yellow flame and a pleasant resin-like, aromatic odor, differing altogether from that of ordinary kerosene. Upon replacing the lamp chimney with one considerably taller, the yellow flame became white and no longer smoked. As the oil was almost free from sulphur, the fraction, up to 300° , was burned without refining at all and seemed to do as well as the refined oil. Still, considering the limited quantity of illuminating oil present, its poor quality and the small amount of asphalt, it would seem that, in the present state of chemical technology, the Breaux Bridge oil is fitted mainly for fuel purposes. For these it is well adapted, containing but little sulphur and being slightly higher in fuel value than the California petroleums, which are now used for fuel in large quantities. Its lubricating qualities have not, as yet, been tested, though it is said to have been used locally with good results.

In order to obtain fractions suitable for combustion, 500 cc. portions were distilled from a liter distilling flask, with the following results:

	Per cent.
Below 220° C.—atmospheric pressure	none
220°-240° C.—atmospheric pressure.....	0.3
240°-260° C.—atmospheric pressure.....	2.
260°-280° C.—atmospheric pressure.....	8.
280°-300° C.—atmospheric pressure.....	6.
300°-320° C.—atmospheric pressure.....	5.
160°-200° C.—at 60 mm. pressure	5.
200°-245° C.—at 60 mm. pressure.....	11.
245°-285° C.—at 60 mm. pressure.....	20.
285°-320° C.—at 60 mm. pressure.....	6.

This was repeated several times until a considerable quantity collected at certain points. The corresponding fractions were then mixed and the series subjected to fractional distillation at 60 mm. It was found exceedingly difficult to obtain a fraction with a constant boiling-point. Portions which came over at, say 165°-167°, would, on redistillation, break up into a series of products, ranging from 150°-180°, the portion remaining in the flask always being darkened and showing some decomposition. After considerable trouble, three fractions were obtained, boiling at 110°-115°, 160°-165°, and 210°-215°, respectively. These were shaken with fuming sulphuric acid, washed with water, sodium hydroxide, and water again, then dried over calcium chloride, and redistilled. In order to prevent decomposition of the higher hydrocarbons, the 210°-215° fraction was dissolved in gasoline before adding the sulphuric acid, and the gasoline subsequently distilled off, as recommended by Mabery and Buck.¹ Each fraction lost considerably on the acid treatment, but the amount was not measured, since so much sulphuric acid was used as to preclude its use, practically, in refining.

The 110°-115° (60 mm.) fraction boiled at 205°-210° at 760 mm., with slight decomposition; it was water-white, and had an odor so strongly resembling turpentine that it was difficult to distinguish them, one from the other. This odor was not affected by the acid treatment. A portion of the oil was polarized, but showed no optical activity. This odor is so marked that a similar distillate, obtained in the Jennings refinery, is now being offered for sale as a turpentine substitute, and the makers claim it answers its purpose well. The specific gravity of the 110°-115° fraction was 0.8479 at 27°. Its molecular weight was determined by the

¹ This Journal, 22, 555.

freezing-point method, benzene being used as a solvent; 161 was found; calculated for $C_{12}H_{22}$, 166. A combustion of the oil gave, for carbon, 86.4 per cent., and for hydrogen, 13.38; calculated for $C_{12}H_{22}$, carbon, 86.74 per cent.; hydrogen, 13.26.

The 160°-165° fraction (60 mm.) was treated in the same way as the preceding one. It had none of the turpentine-like odor. Its specific gravity at 29° was 0.8785. Its molecular weight, by the freezing-point method, with benzene, was 189; calculated for $C_{14}H_{26}$, 194. On combustion it gave, for carbon, 86.79 per cent., and for hydrogen, 13.1. Calculated for $C_{14}H_{26}$, carbon, 86.59 per cent.; hydrogen, 13.41.

The 210°-215° fraction (60 mm.) was treated as was the preceding. Its specific gravity at 29° was 0.9009. Its molecular weight, by the freezing-point method, was 233; calculated for $C_{17}H_{30}$, 234. Upon combustion it gave, for carbon, 87.15 per cent., and for hydrogen, 12.72 per cent. Calculated for $C_{17}H_{30}$, carbon, 87.18 per cent.; hydrogen, 12.82 per cent.

From the above figures it is evident that the series C_nH_{2n-2} and C_nH_{2n-4} are the main constituents of this oil. This corresponds with the conclusions reached by Mabery and Buck¹ on some Texas oil, and also by Mabery² on the Beaumont oil. Mabery considers the series C_nH_{2n-2} as belonging to the dicyclic polymethylene series, in which view Richardson and Wallace concur. By analogy, the series C_nH_{2n-4} might be looked upon as being desired from dihexahydrofluoren, $C_6H_{10}-C_6H_{10}$; but there



is, as yet, little positive evidence as to the structure of either series. They are almost certainly not unsaturated aliphatic compounds, however, for they do not behave as though unsaturated. If they are cyclic compounds, they might respond to Nikiforoff's methods of consecutive decomposition under increased pressure, which has succeeded in producing benzene derivatives of excellent quality from Russian petroleum. That Louisiana petroleum does undergo progressive decomposition, under continued distillation, has been established in the course of this investigation.

¹ *Loc. cit.*

² This Journal, 1901, p. 264.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 90.]

ON THE INFLUENCE OF DIET, MUSCULAR EXERTION AND LOSS OF SLEEP UPON THE FORMATION OF URIC ACID IN MAN.

BY H. C. SHERMAN.

Received September 11, 1903.

WITHIN the last few years much attention has been given to the behavior of the nucleins and purin bodies in the human organism, and the sources and significance of the uric acid eliminated. This work has been so fully discussed by recent writers,¹ that it is unnecessary to review it here. The principal workers are agreed that the uric acid eliminated comes, in part, from the activities within the body and, in part, from the purin bodies ingested, either as such or as constituents of the nucleins, the former being sometimes called the "endogenous," the latter the "exogenous" uric acid. No general agreement exists, however, in regard to the causes or limits of variation in either the endogenous or the exogenous portion. The daily elimination of uric acid by healthy men, on diets believed to be practically free from purin bodies, has been variously reported at from 0.20 to 0.60 gram. Burian and Schur hold that this variation in the endogenous uric acid is a matter of individual peculiarity, but that the exogenous portion bears quantitative relations to the different purin compounds of the ingested foods. Other investigators have failed to confirm the latter claim and hold that this exogenous portion is also influenced by other causes. Evidently these questions can only be settled by the accumulation of data regarding the influence of various conditions upon the elimination of uric acid by different healthy men.

Some years ago, in connection with a study belonging to the nutrition investigations of the United States Department of Agriculture,² the writer had opportunity to determine the uric acid eliminated by professional bicycle riders during a six-day race, involving such severe and long-continued exertion as would only be possible for well-trained athletes of unusual strength and en-

¹ Burian and Schur: *Archiv. für ges. Physiol. (Pflüger)*, 80, 241; 87, 239; 94, 273. Loewi: *Archiv. experimen. Path. and Pharm.*, 44, 1; 48, 157. Weiner's "Ergebnisse der Physiologie," 1902.

² U. S. Dept. of Agr., Office of Experiment Stations, Bull. 98. "The Effect of Severe and Prolonged Muscular Work upon Food Consumption, Digestion and Metabolism," by W. O. Atwater and H. C. Sherman.

duration. The subjects rode usually about twenty hours per day, sleeping only one or two hours in every twenty-four, and the food consumed was large in amount and, in some cases, contained large quantities of meat extract. As there was no opportunity to experiment with these subjects, except during the race, it was impossible to judge in how far the results of muscular exertion were complicated by those of diet and loss of sleep, and the figures for uric acid were, therefore, not published. Since that time it has been possible to experiment with another subject regarding the influence of loss of sleep, as well as with some of the foods used by the racers, and it is believed that the results can now be interpreted with sufficient accuracy to render them of value.

OBSERVATIONS UPON PROFESSIONAL BICYCLE RACERS.

A detailed description of the subjects and their work, diet and metabolism will be found in the bulletin cited above. The principal data bearing upon the present discussion, may be summarized as shown on pages 1161 and 1162.

It will be noted that large amounts of food were consumed and large quantities of nitrogen eliminated. The elimination of uric acid was not, as a rule, increased in proportion to the total nitrogen, but was in most cases somewhat and in some cases considerably above the normal. Before considering whether this increase of uric acid should be attributed to the diet or the work, the possible influence of loss of sleep may be noted.

INFLUENCE OF LOSS OF SLEEP.

In connection with certain experiments with another subject, "S," the details of which are described elsewhere,¹ the uric acid elimination was observed for a period of several days, the diet being kept constant and all the conditions as nearly uniform as possible, except that during three consecutive days the amount of sleep was materially reduced. The food of each day consisted of 300 grams bread (soda-crackers), 2,040 grams milk, and 40 grams butter. The principal results are given on page 1163.

¹ U. S. Dept. of Agr., Office of Experiment Stations, Bull. 121. "Experiments upon the Metabolism of Nitrogen, Sulphur and Phosphorus in the Human Organism."

Subject.	Day of race.	Sleep (about). Hrs. and min.	Distance ridden. Miles.	Food consumed.	Nitrogen in urine. Grams.	Uric acid in urine. Grams. ²
"M"	1 ¹	0:0	441.8	{ Eggs, 43 grams; milk and kumyss, 7828 grams; boiled rice, 360 grams; sugar, 72 grams; fruit, 480 grams.	35.1	1.00.
	2	1:40	366.7	{ Meat extract, 127 grams; eggs, 173 grams; milk and kumyss, 3261 grams; boiled cereals, 643 grams; sugar, 92 grams; fruit, 999 grams.	42.7	1.07
	3	1:35	334.1	{ Meat extract, 311 grams; milk, 4937 grams; bread, 35 grams; boiled cereals, 877 grams; pastry, 142 grams; sugar, 53 grams; fruit, 2003 grams.	46.2	1.50
	4	1:10	316.5	{ Meat extract, 43 grams; milk and matzoon, 1057 grams; rice pudding, 737 grams; pastry, 71 grams; fruit, 1459 grams.	35.7	1.71
	5	1:5	327.8	{ Meat extract, 9 grams; eggs, 94 grams; milk, 823 grams; soup, 113 grams; boiled cereals, 386 grams; sugar, 25 grams; pastry, 1009 grams; fruit, 870 grams.	30.7	1.15
	6	2:30	220.5	{ Meat extract, 5 grams; milk, 1985 grams; boiled rice, 422 grams; pastry, 1189 grams; sugar, 19 grams; fruit, 2161 grams.	26.9	1.00
"P"	1 ¹	?	863.2	{ Eggs, 79 grams; milk and kumyss, 6122 grams; boiled cereals, 1080 grams; sugar, 89 grams; fruit, 19 grams.	32.8	0.62
	2	?		{ Meat extract, 85 grams; eggs, 46 grams; milk and kumyss, 4729 grams; boiled cereals, 887 grams; sugar, 85 grams; fruit, 255 grams.	43.6	0.84
	3	?		{ Meat extract, 156 grams; butter, 28 grams; milk and kumyss, 4340 grams; bread, 307 grams; boiled cereals, 1118 grams; sugar, 80 grams; fruit, 235 grams.	40.3	1.06
"A"	1	0:0	402.0	{ Meat, 85 grams; beef tea, 440 grams; eggs, 241 grams; milk, 531 grams; malted milk, 91 grams; jelly, 42 grams; bread, 459 grams; boiled cereals, 935 grams; sugar, about 200 grams; fruit, 434 grams.	25.3	0.88

¹ Subjects "M" and "P" dined heartily upon beefsteak about two hours before the beginning of the race.

² Determined by the Ludwig-Salkowski method.

Subject.	Day of race.	Sleep (about). Hrs. and min.	Distance. ridden. Miles.	Food consumed.	Nitrogen in urine. Grams.	Uric acid in urine. Grams.
"A"	2	1:30	371.3	{ Meat, 148 grams; broth, 170 grams; beef juice, 128 grams; butter, 64 grams; eggs, 57 grams; milk, 116 grams; malted milk, 82 grams; jelly, 99 grams; bread, 204 grams; boiled cereals, 347 grams; sugar, about 250 grams; fruit, 1195 grams.	32.8	0.90
	3	0:20	352.7	{ Meat, 149 grams; meat extract, 24 grams; broth, 283 grams; eggs, 369 grams; butter, 78 grams; milk, 142 grams; malted milk, 78 grams; jelly, 213 grams; soup, 191 grams; bread, 361 grams; boiled cereal, 532 grams; sugar about 400 grams; fruit, 933 grams; cocoa wine, 170 grams.	39.0	1.08
	4	2:0	285.3	{ Meat, 206 grams; meat extract, 43 grams; broth, 879 grams; eggs, 283 grams; butter, 198 grams; milk, 312 grams; malted milk, 36 grams; jelly, 269 grams; bread, 659 grams; sugar, about 300 grams; fruit, 928 grams; cocoa wine, 198 grams.	65.1	2.50
	5	3:40	229.4	{ Meat, 326 grams; broth, 305 grams; eggs, 56 grams; butter, 220 grams; milk, 149 grams; malted milk, 21 grams; jelly, 156 grams; bread, 709 grams; tapioca pudding, 170 grams; sugar, about 300 grams; fruit, 1495 grams; cocoa wine, 43 grams.		
	6	2:0	181.9	{ Meat, 220 grams; broth, 701 grams; eggs, 114 grams; butter, 92 grams; milk, 269 grams; malted milk, 7 grams; jelly, 220 grams; bread, 496 grams; tapioca pudding, 142 grams; sugar, about 330 grams; fruit, 673 grams; cocoa wine, 113 grams.	39.8	1.63

Days.	Sleep (about). Hours.	Amount of urine. Grams.	Nitrogen in urine. Grams.	P ₂ O ₅ in urine. Grams.	Uric acid in urine. ¹ Gram.
1	7	817	15.38	2.98
2	7	902	13.89	3.07
3	7	993	14.28	3.21	0.37
4	7	838	13.68	3.23	0.32
5	2½	852	13.96	2.94	0.36
6	4	782	14.04	3.07	0.34
7	0	851	15.63	3.28	0.34
8	7½	966	15.06	3.80	0.30
9	7½	1160	15.65	3.46	0.31
10	7	978	13.67	3.07	0.34
11	7	952	13.51	2.89	0.32
12	7	1001	13.82	3.21	0.30

From this it would appear that the loss of sleep had little, if any, influence upon the elimination of uric acid.

INFLUENCE OF DIET AND MUSCULAR WORK.

While there is no question that the different nitrogenous bodies of the food differ greatly in their effect upon uric acid formation and that very little uric acid is formed on a diet of such foods as bread, milk, butter and eggs, it is still uncertain whether the uric acid output is entirely independent of the quantity of such foods consumed. The results of two series of observations upon subject "S," bearing upon this point, may be summarized as follows:

INFLUENCE OF VARYING AMOUNTS OF BREAD AND MILK.

Days.	Amount of urine. Grams.	Nitrogen in urine. Grams.	P ₂ O ₅ in urine. Grams.	Uric acid in urine. Gram.	Food per day.
1	681	11.65	1.92	0.42	Bread ("soda-crackers"), 150 grams; milk, 1500 grams.
2	605	11.12	2.02	0.35	
3	620	11.35	2.27	0.37	
4	566	11.66	2.33	0.38	
5	555	11.75	2.29	0.38	
6	687	14.83	2.73	0.44	Bread ("soda-crackers"), 300 grams; milk, 3000 grams.
7	874	15.81	3.28	0.41	
1	... ²	Bread ("soda-crackers"), 405 grams; milk, 1000 grams; butter, 60 grams.
2	609	10.19	2.15	0.32	
3	711	10.92	2.43	0.37	
4	670	10.17	2.34	0.33	
5	2180	15.12	3.39	0.33	Bread ("soda-crackers"), 120 grams; milk, 3060 grams.
6	2130	16.07	3.94	0.34	
7	1859	16.98	4.10	0.34	

¹ The figures for uric acid given in this and the following table were determined by Folin's modification of the Hopkins method.

² Sample lost.

In the first series, where the change consisted in doubling the amounts of bread and milk consumed, the relative proportions remaining the same, there appears to be a slight increase in the uric acid elimination. In the second series, where the diet was changed by omitting the butter, reducing the bread and greatly increasing the milk consumed, thus giving a large increase in the protein of the diet with but little change in the fuel value, the amount of uric acid eliminated remained practically unchanged.

The fact that the slight increase found in the first series does not appear in the second, may be taken as an indication either that the increase was due to the superabundance of the diet as a whole, rather than to the increased consumption of protein alone, or that the purin bodies, while occurring only in very small quantities in either, were relatively more abundant in the bread than in the milk. The latter seems probable, inasmuch as the quality of flour used in making "soda-crackers" might easily contain some of the germ of the wheat. In either case it would appear that even a diet of bread and milk introduces a certain amount of "exogenous" purin bodies, though this amount is doubtless quite small.

The large quantities of uric acid eliminated by the professional bicycle racers may, therefore, to some extent, be attributed to the mere abundance of the diet. To a much greater extent, however, it is doubtless due to the quantities of meat extract consumed. During a two days' experiment, the attempt was made by subject "S" to consume such quantities of meat, meat extract and fruit (together with bread and milk) as would be comparable with those found in the dietaries of two of the racers.¹ The food consumed by "S" during the two days was about as follows: Meat, 400 grams; meat extract, 100 grams; milk, 2000 grams; bread, 350 grams; fruit, 800 grams. Except as regards the quantities of cereal and milk products, this dietary is not greatly different from the average for subjects "M" and "P" during the first two days of the bicycle race, including the meat consumed by these subjects just before the beginning of the observations.

The principal source of purin bodies was, of course, the meat extract, a concentrated commercial preparation called "Vigoral."

¹ On account of the great variety of foods consumed by subject "A" and the fact that he took cocoa wine and, during the last days, small quantities of strychnine, no direct comparison with this subject was attempted.

"M" and "P" consumed respectively 127 and 85 grams (average 106 grams), while "S" consumed 100 grams of the same preparation. "S" eliminated, during the two days, 1.66 grams of uric acid, or 0.83 gram per day; "M" and "P" together 3.53 grams, or an average of 0.88 gram per day. This difference is hardly greater than would be expected from the large quantities of cereals and milk consumed by the latter subjects. Hence, in so far as this method of comparison is applicable, it would indicate that, at least during the early days of the race, the uric acid elimination of these athletes was only such as would naturally result from the food consumed and was not appreciably increased by the muscular work performed.

In another experiment, "S," who at this time was living upon a diet of cereals and milk, and had taken but little exercise for three or four weeks, walked two and one-half hours over country roads at the rate of four and one-half miles per hour and during the following two and one-half hours practiced, at intervals, an exercise consisting in raising and lowering the body by means of the arms. Nearly all of the muscles were thus exercised, and while the work performed was not large in actual amount, the exertion was sufficient to keep the pulse rate at 100 to 125 for about five hours and to cause a feeling of fatigue during the remainder of the day. The exercise was followed by an increase in the uric acid output of about 0.15 gram during the day of exercise and the day following. This result is in harmony with that reached by Dunlop, Paton, *et. al.*,¹ who found an increased elimination of uric acid after muscular exercise when the subject was in poor, but not when it was in good, training.

SUMMARY.

Without attempting a full discussion of the data here given, which would involve a review of the recent extensive investigations already mentioned, the principal points of interest may be summarized as follows:

Both with professional athletes and with the subject of sedentary habits, the elimination of uric acid was primarily dependent upon the food consumed.

While very small changes, apparently, resulted from large variations in the amount of a bread-and-milk diet, the elimination

¹ *J. Physiol.*, 22, 68.

of uric acid was mainly determined by the quantities of meat products consumed.

In the case of well-trained professional athletes, very severe and prolonged muscular exertion had little influence upon the formation and elimination of uric acid, except indirectly, by inducing an appetite for stimulating foods such as meat extracts.

Marked loss of sleep had no apparent influence upon the amount of uric acid eliminated.

The writer desires to express his indebtedness to Professor W. O. Atwater, of Wesleyan University, in whose laboratory a large part of the work, here described, was performed.

NEW YORK CITY,
September, 1903.

[CONTRIBUTIONS FROM THE UNIVERSITY OF ILLINOIS, AGRICULTURAL
EXPERIMENT STATION, NO. 10.]

THE CHEMICAL COMPOSITION OF DIFFERENT PARTS OF THE CORN¹ KERNEL.²

BY C. G. HOPKINS, L. H. SMITH, AND E. M. EAST.

Received September 4, 1903.

THE possibility of selecting seed corn for improved chemical composition by a simple mechanical examination of sections of kernels has been clearly established by experiments previously reported;³ and the practical value of this method of selecting seed corn for high protein, high oil, and other desirable qualities, has been fully confirmed by subsequent investigations.⁴

A considerable amount of additional data relating to this matter has been accumulating with the progress of our experiments in corn-breeding, and because of the very great importance of this subject to agriculture, and also because of the marked interest which is manifested both by progressive, practical agriculturists and by scientific investigators, it has seemed advisable to publish, in somewhat greater detail, the results of our investigations along this line.

¹ "Corn" is, of course, used with the American meaning of Indian corn or maize.

² From advance sheets of Bulletin No. 87 of the University of Illinois Agricultural Experiment Station.

³ This Journal 21, 1039 (1899); Univ. of Ill. Agr. Expt. Station Bulletin 55 (1899).

⁴ Univ. of Ill. Agr. Expt. Station Bulletin 82 (1902); U. S. Dept. of Agr., Office of Expt. Stations, Bulletin 123, 91 (1903); West Indian Bulletin 4, 9 (1903).

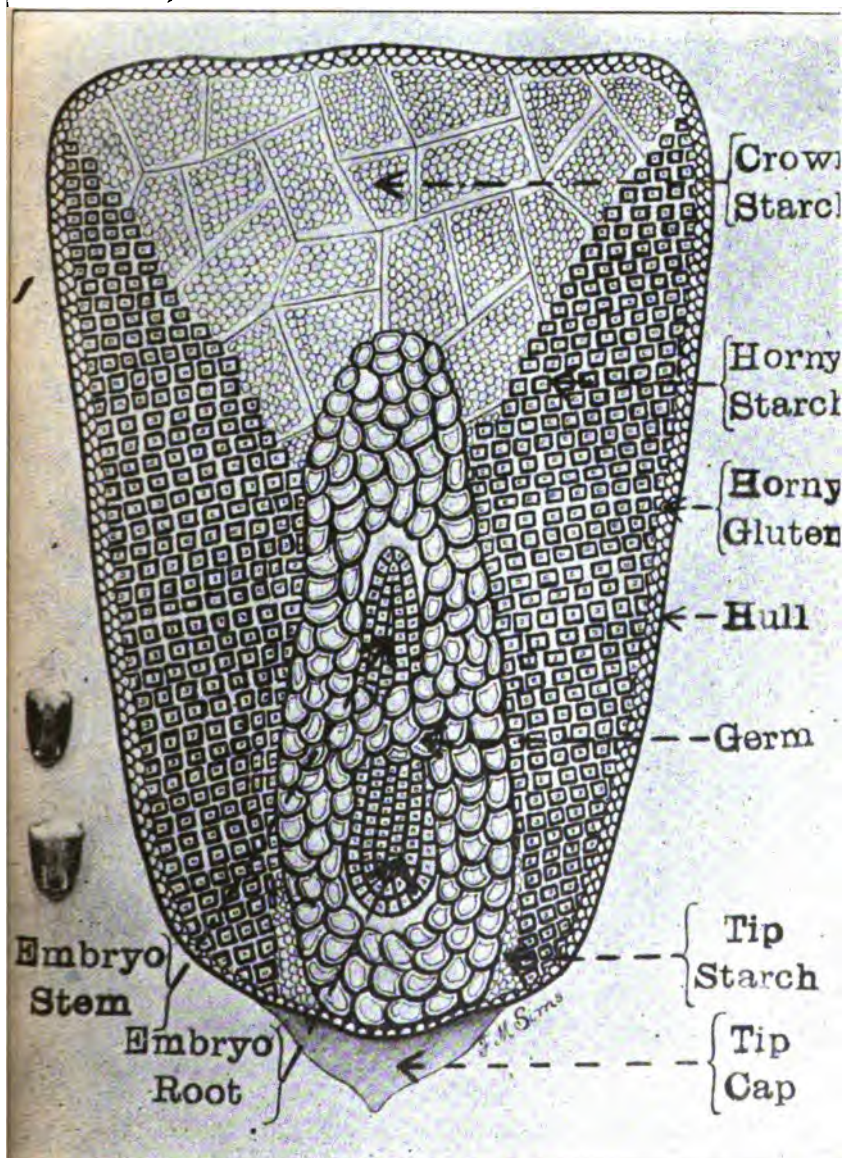


Plate I.—Low-protein corn kernel from drawing (small kernels from photograph)

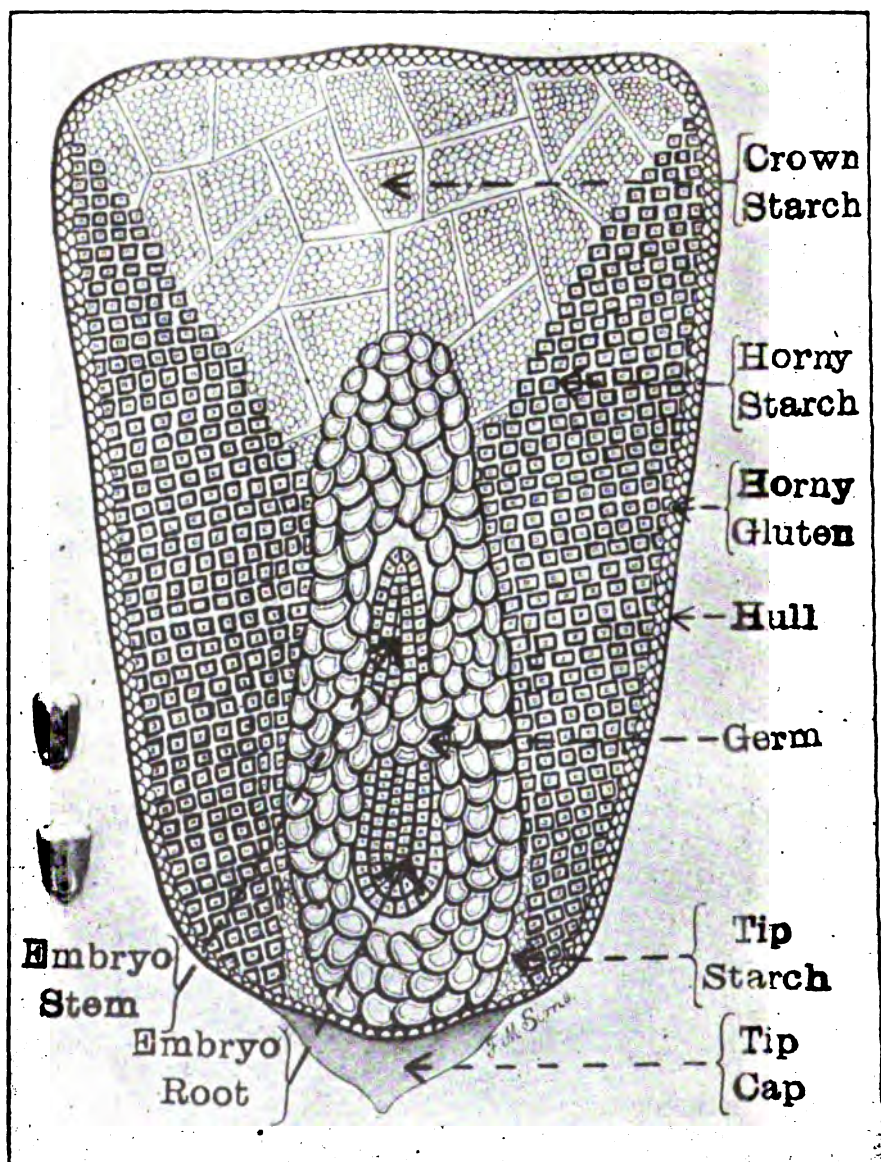


Plate II.—High-protein corn kernel from drawing (small kernels from photograph).

PARTS OF THE CORN KERNEL.

There are six distinctly different parts in a kernel of corn, as will be readily seen by the reference to Plates¹ I and II.

(1) *Tip Cap*.—This is a small cap, covering the tip end of the kernel, and serves as a protection to the end of the germ. It consists of material somewhat resembling the cob, and occasionally, in shelling corn, the tip cap remains attached to the cob, leaving the tip end of the germ uncovered, but nearly always it remains on the kernel.

(2) *Hull*.—This is the very thin outer covering of the kernel. It consists largely of carbohydrates, especially fiber or cellulose, although it also contains a small percentage of other constituents.

(3) *Horny Glutinous Part*.—This part is the aleurone layer which lies immediately underneath the hull. It constitutes a second covering of the kernel, usually much thicker than the hull. For short, it is called *horny gluten*, although it is, of course, not pure gluten. However, it is the richest in protein of any part of the corn kernel, as has been stated in bulletins published by this station and previously by Dr. Voorhees, director of the New Jersey Experiment Station.

(4) *Horny Starchy Part*.—This part lies next to the horny gluten, on the back and sides of the kernel. For short, it is called *horny starch*, although it is not pure starch, as it contains considerable amounts of other constituents, especially of protein. In an examination of the kernel with the unaided eye, the horny glutinous part and the horny starchy part are not readily distinguished from each other, the line between them being somewhat indefinite and indistinct. Considered both together, these two parts constitute the horny part of the kernel.

(5) *White Starchy Part*.—This part occupies the crown end of the kernel above the germ and it also nearly surrounds the germ toward the tip end of the kernel. For convenience, this material is called *white starch*, although it is not pure starch. In some kernels the horny starch extends nearly or quite to the germ (near the middle of the kernel) and thus separates more or less completely the white starch into two parts which we call *crown starch* and *tip starch*.

¹ It should be understood that these drawings are intended to show merely the location and relative amounts of the various parts of the kernel, not the exact cell structure.

(6) *Germ*.—The germ occupies the center of the front of the kernel toward the tip end and usually extends about one-half or two-thirds of the length of the kernel. Within the body of the germ are the embryo stem pointing upward toward the crown end and the embryo root pointing downward toward the tip of the kernel, both of which are, of course, parts of the germ. These embryo parts within the germ may be easily seen by any one who will carefully shave off the front side of the germ from a kernel of corn (see small photographic reproduction of sections of kernels of high- and low-protein corn in Plates I and II).

MECHANICAL SEPARATION OF THE DIFFERENT PARTS.

It is not a difficult matter to obtain very pure samples of each of the above-named parts of the corn kernel, although in making the separations there is, of necessity, some waste material consisting of a mixture of three different parts; namely, horny gluten, horny starch, and white starch.

By the use of a small, sharp knife, any one can make the following separations: (1) Tip cap; (2) hull; (3) horny gluten; (4) horny starch;¹ (5a) crown starch; (5b) tip starch; (6) germ; (7) waste (mixed material). In making these separations the kernels are first soaked in hot water for fifteen or twenty minutes.

The tip cap is then very easily and perfectly separated by simply cutting under one edge and then pulling it off. The hull is separated without difficulty by peeling it off in strips. It is only necessary to use the knife to start the peeling at the tip end where the hull has been broken by removing the tip cap. With some care the hull can be completely peeled out of the dent in the corn. The aleurone layer is more easily distinguished after the hull is removed. It covers the entire kernel, excepting the germ.² The aleurone layer is removed by carefully shaving it off with a sharp knife. Adhering particles of starch can be more easily separated from this horny gluten after the shavings have been allowed to dry for some time. In scraping off these particles of horny starch or white starch adhering to the shavings, more or less horny gluten will also be scraped off, so that, while we are thus able to obtain a pure, clean sample of the aleurone layer, we

¹ As used in this article the term "starch" is employed in a technical or commercial sense, and not as the name of a definite chemical compound.

² This layer does not occur between the germ and the tip cap as indicated in the drawings.

also obtain some waste material, consisting of particles of horny gluten, horny starch, and white starch.

The germ is next removed, and with care this can be done very perfectly. If any particles of starch adhere to the germ they can easily be completely removed. After the tip cap, hull, aleurone layer, and germ have been removed, the remainder of the kernel, consisting of the horny starch and white starch only, is allowed to dry, and the kernel is broken in two lengthwise.

The crown starch is dug out with the knife as completely as possible without taking any of the horny starch. The tip starch is next removed in the same manner as the crown starch.¹ The horny starch from each side usually remains in a solid piece. This is now carefully scraped to remove all adhering particles of white starch or horny gluten, the scrapings being carefully saved and added to the waste material.

By this method of separation we obtain eight different products, including the waste material, and seven of these products are pure samples of distinctly different parts of the corn kernel, excepting the crown starch and tip starch, both of which, of course, belong to the white starch; they are kept separate, however, because they are found in different places, frequently being entirely separated in the kernel, although more commonly there is some white starch continuous from crown to tip.

COMPOSITION OF THE DIFFERENT PARTS.

Table I shows the percentage of these eight different products, or parts, and the percentage composition of each part, also the percentage composition of the whole corn, for each of three different ears of corn. Ear No. 1 is corn of comparatively low¹ protein content. Ear No. 2 has about the usual protein content of ordinary corn. Ear No. 3 is high¹ protein corn. About 200 grams (nearly one-half pound) of kernels from each ear were separated into the different parts, and each part was then weighed and

¹ It should be understood that ear No. 1 (9.28 per cent. protein) and ear No. 3 (12.85 per cent. protein) do not represent extremes in protein content; indeed, in our breeding of corn for low protein we have produced good ears containing less than 6.50 per cent. of protein, and in our high-protein field we have produced corn containing over 16 per cent. of protein. In extremely low-protein corn the percentage of horny part is very much less than in ear No. 1, and in extremely high protein corn the tip white starch is frequently almost entirely wanting and the crown white starch very greatly reduced, both being replaced by the horny part, as shown in the drawings and also in the actual photographs of sections of kernels shown beside the drawings in Plates I and II.

analyzed separately, another sample of the corn from each ear being analyzed to give the composition of the whole corn. (All results are given on the water-free basis.)

TABLE I.—PERCENTAGE OF DIFFERENT PARTS AND PERCENTAGE COMPOSITION OF EACH PART.

Ear No. 1 (low in protein).

Names of parts.	Per cent. of whole.	Composition of parts.			
		Protein. Per cent.	Oil. Per cent.	Ash. Per cent.	Carbohydrates. Per cent.
Tip caps	1.20	7.36	1.16	0.91	90.57
Hulls	5.47	4.97	0.92	0.82	93.29
Horny gluten	7.75	19.21	4.00	0.92	75.87
Horny starch	29.58	8.12	0.16	0.18	91.54
Crown starch.	16.94	7.22	0.19	0.32	92.27
Tip starch.....	10.03	6.10	0.29	0.29	93.31
Germes	9.59	19.91	36.54	10.48	33.07
Mixed waste	18.53	9.90	1.06	0.61	88.43
Whole corn	9.28	4.20	1.41	85.11

Ear No. 2 (medium in protein).

Tip caps.....	1.46	8.83	2.30	1.11	87.76
Hulls.....	5.93	3.96	0.89	0.79	94.36
Horny gluten	5.12	22.50	6.99	1.72	69.09
Horny starch.....	32.80	10.20	0.24	0.24	89.32
Crown starch.....	11.85	7.92	0.17	0.24	91.67
Tip starch.....	5.91	7.68	0.39	0.31	91.62
Germes	11.53	19.80	34.84	9.90	35.46
Mixed waste	25.40	11.10	1.23	0.57	87.10
Whole corn	10.95	4.33	1.55	83.17

Ear No. 3 (high in protein).

Tip caps	1.62	4.64	1.99	1.87	91.50
Hulls.....	6.09	3.84	0.76	1.10	94.30
Horny gluten	9.86	24.58	4.61	1.74	69.07
Horny starch.....	33.79	10.99	0.22	0.21	88.58
Crown starch.....	10.45	8.61	0.52	0.37	90.50
Tip starch.....	6.23	7.29	1.36	0.60	90.75
Germes	11.93	19.56	33.71	10.00	36.73
Mixed waste	20.03	12.53	1.15	0.61	85.71
Whole corn	12.85	5.36	1.67	80.12

A careful study of Table I reveals some very interesting and useful facts regarding the structure of the corn kernel and the composition of the different parts. It is exceedingly useful to be able, by a mechanical examination of corn, not only to pick out high-protein corn or high-oil corn as one may desire, but even to separate the several distinctly different parts from one another

by purely mechanical means—to separate, for example, the aleurone layer, containing (in the high-protein ear) nearly 25 per cent. of protein, and then the white starchy parts, with only 7 or 8 per cent. of protein; or the germs containing about 35 per cent. of oil and 10 per cent. of ash, and then the horny starchy part containing less than 0.25 per cent. of either oil or ash.

The hulls contain about 4 per cent. of protein and are clearly the poorest in protein of any part of the kernel, the next poorest being the tip caps and white starchy parts, containing about 7 or 8 per cent., the tip starch being slightly poorer than the crown starch. The horny starch is richer in protein than the white starch, especially in the medium and high protein corn where the difference amounts to more than 2 per cent., the horny starchy part containing from 10 to 11 per cent. of protein. The protein content of the germs is very uniform in the different ears, although the poorest germs are found in the high-protein corn, and the richest in the low-protein corn, the variation being from 19.56 to 19.91 per cent. The aleurone layer is the richest in protein of any part of the kernel in both ordinary and high-protein corn, as was pointed out several years ago by Dr. Voorhees,¹ director of the New Jersey Experiment Station, and as we have quoted in previous publications of the Illinois Experiment Station. In the high-protein corn the protein content of the aleurone layer amounts to 24.58 per cent. In the low-protein corn it is slightly less than that of the germ.

It is plainly seen that the oil in corn is very largely in the germ, although the aleurone layer also contains a considerable percentage, the germ containing about 35 per cent. of oil and the aleurone layer about 5 per cent. Both the horny starch and the white starch are exceedingly poor in oil, averaging about 0.25 per cent., if we disregard the tip starch in ear No. 3, which appears to have absorbed some oil directly from the germ which it adjoins and partially surrounds. The hulls contain slightly less than 1 per cent. of oil and the tip caps slightly more than 1 per cent., and it is quite possible that this oil may have been obtained, in part at least, by absorption from the aleurone layer and germ. Indeed, it seems highly probable that practically all of the true oil in the corn kernel is originally deposited in the germ and aleurone layer.

¹ New Jersey Agricultural Experiment Station Bulletin 108 (1894).

and that the small percentage or mere trace, which is found in the other parts, is largely obtained by absorption. That such absorption actually does occur is definitely proved by the fact that the percentage of oil in hominy and hominy products increases with the age of the corn used in the milling. (Hominy consists largely of the horny starch with more or less adhering white starch.)

It may be of interest to state in this connection that in 1866 Haberlandt¹ discovered, with the microscope, that the germ of the corn kernel contains a large amount of oil. He observed no oil in the remaining portions of the kernel. By chemical analysis, Lenz¹ found, however, that after the germs were removed the remaining portion of the kernel contained 1.57 per cent. of oil. These results were fully confirmed by Dr. Atwater,² who found 1.63 per cent. of oil in the corn after removing the germs and adjoining material, although neither Lenz nor Atwater appear to have ascertained that the horny gluten (the aleurone layer) contains the chief percentage of oil outside of the germ.

By further reference to Table I, it will be observed (1) that the germ contains about 10 per cent. of ash or mineral matter; (2) that this is about ten times the average percentage of ash contained in the other parts; and (3) that the percentage of ash in the different parts varies with the percentage of oil, to quite a noticeable degree. Of course, the percentage of carbohydrates (starch, cellulose, pentosans, etc.) varies inversely as the sum of the other constituents, being about 35 per cent. in the germ, 70 per cent. in the horny gluten, and from 90 to 95 per cent. in the other principal parts.

The marked degree of uniformity in the entire percentage composition of the germs from each of these three ears, whether low-protein, medium-protein, or high-protein, seems especially noteworthy. The percentage of protein varies only from 19.56 to 19.91; the oil from 33.71 to 36.54; the ash from 9.90 to 10.48; and the carbohydrates from 33.07 to 36.73. It will also be noted that the percentages of both protein and oil are lower in the germs from high-protein corn than in those from the low-protein corn, although the differences are not marked.

¹ *Allgemeine land- und forstwirtschaftliche Zeitung*, 1866, p. 257; *Jahresbericht (Hofmann) über die Agricultur-Chemie*, 9, 106 (1866).

² *Thesis*, Yale College (1869); *Am. J. Sci. and Arts* (2), 48, 352 (1869).

MATHEMATICAL DISTRIBUTION OF WASTE.

It will be borne in mind that in making the mechanical separations, in order to obtain each of the seven different parts in pure condition, unmixed with any other part, there was necessarily some waste product. This waste substance amounted to about 20 per cent. of the whole. As has already been explained, this mixed waste material consists of only three distinctly different parts—horny gluten, horny starch, and white starch (from crown and tip), the other three parts—tip caps, hulls, and germs—being easily separated completely and in pure form.

By a simple computation the mixed waste material can be distributed among the respective parts of which it is composed, provided we may be allowed to make the assumption (which is approximately the truth) that the horny starch and white starch are present in the waste material in the same proportions as they are in the pure separated portions. Any error which might be introduced by following this assumption would have but little effect because the composition of the horny starch and white starch are not very markedly different (the protein differs by 2 to 3 per cent.) ; and also because the total amount of waste material to be distributed is only from one-third to one-half the sum of the separated horny starch and white starch.

It will be observed (see Table I) that the mixed waste is always richer in protein than the horny starch, thus showing that, besides horny starch and white starch, it also contains more or less horny gluten, which, of course, we know to be the fact.

If in 100 grams of corn we let x equal the number of grams of tip starch, Bx the number of grams of crown starch, Cx the number of grams of horny starch, y the number of grams of horny gluten, and S the sum of these four parts, then

$$x + Bx + Cx + y = S. \quad (1)$$

Now if we let a equal the per cent. of protein in the tip starch, b the per cent. of protein in the crown starch, c the per cent. of protein in the horny starch, d the per cent. of protein in the horny gluten, and s the number of grams of protein in all of these four parts, then

$$ax + bBx + cCx + dy = s. \quad (2)$$

Thus we have two equations with which to solve for x and y , which are the only unknown quantities, B and C being factors

which can be obtained by dividing the per cent. of separated crown starch and horny starch, respectively, by that of tip starch, and S being the sum of the separated tip starch, crown starch, horny starch, horny gluten and mixed waste, as given in Table I, and a, b, c, d being the respective percentages of protein in the four separated materials, tip starch, crown starch, horny starch, and horny gluten, and s being the total number of grams of protein contained in these four separated parts and in the mixed waste, all of which data are also given in Table I.

PHYSICAL COMPOSITION OF THE CORN KERNEL.

From the above computations we obtain the results given in Table II, which gives the total percentages of each of the seven different parts contained in the corn kernel (counting crown starch and tip starch as two parts), and with no waste material.

TABLE II.—TOTAL PERCENTAGES OF THE DIFFERENT PARTS OF THE CORN KERNEL.

Name of parts.	Ear No. 1 (low- protein).	Ear No. 2 (medium- protein).	Ear No. 3 (high- protein).
Tip caps	1.20	1.46	1.62
Hulls	5.47	5.63	6.09
Horny gluten.....	11.61	8.51	13.32
Horny starch	37.15	47.08	44.89
Crown starch.....	21.26	17.01	13.88
Tip starch.....	13.71	8.48	6.28
Germs	9.59	11.53	11.93
Total.....	99.99	100.00	100.01

It will be observed that the percentages of horny gluten, horny starch, and germs are noticeably higher in the high-protein corn than in the low-protein corn, while the opposite is true with the white starch, the percentages of crown starch and tip starch being markedly higher in the low-protein corn than they are in the high-protein corn. It is noteworthy that the horny gluten in high-protein corn not only contains a higher percentage of protein than the germs, but that the proportion of horny gluten in the kernel equals or exceeds that of the germs. The only discrepancies appearing in Table II are the low percentage of horny gluten and the high percentage of horny starch in ear No. 2. Otherwise the percentages of parts in the medium-protein ear are always intermediate between those in the other two ears, as would be expected. Even these discrepancies disappear if the two

Ear No. 2 (medium in protein).

Names of parts.	Physical distribution (grams or pounds).	Chemical composition.			
		Protein (grams or pounds).	Oil (grams or pounds).	Ash (grams or pounds).	Carbohydrates (grams or pounds).
Tip caps	1.46	0.13	0.03	0.02	1.28
Hulls	5.93	0.23	0.05	0.05	5.60
Horny gluten	8.51	1.89	0.59	0.15	5.88
Horny starch.....	47.08	4.80	0.11	0.11	42.05
Crown starch.....	17.01	1.35	0.03	0.04	15.59
Tip starch.....	8.48	0.65	0.03	0.03	7.77
Germes	11.53	2.28	4.02	1.14	4.09
Total	100.00	11.33	4.86	1.54	82.26
Whole corn	10.95	4.33	1.55	83.17

Ear No. 3 (high in protein).

Tip caps	1.62	0.08	0.03	0.03	1.48
Hulls	6.09	0.23	0.05	0.07	5.74
Horny gluten	13.32	3.27	0.61	0.23	9.20
Horny starch.....	44.89	4.93	0.10	0.09	39.76
Crown starch.....	13.88	1.20	0.07	0.05	12.56
Tip starch	8.28	0.60	0.11	0.05	7.51
Germes	11.93	2.33	4.02	1.19	4.38
Total	100.01	12.64	4.99	1.71	80.63
Whole corn.....	12.85	5.36	1.67	80.12

The agreement between the sum of the separate determinations and the direct determinations of the same constituent in the whole corn is very satisfactory, considering that these results are obtained by computation from the analyses of nine different materials, including the whole corn. The greatest difference is well within the limit of unavoidable error in sampling and analytical determinations. A careful study of this table will reveal some interesting and valuable facts. For example, it will be seen that in 100 pounds of the low-protein corn the horny gluten contains only 2.23 pounds of protein, while 3.27 pounds of protein are contained in the horny gluten in 100 pounds of the high-protein corn. Again, in 100 pounds of the low-protein corn the horny starch contains only 3.02 pounds of protein, while 4.93 pounds of protein are contained in the horny starch in 100 pounds of the high-protein corn.

On the other hand, in 100 pounds of the low-protein corn, the crown starch and tip starch contain 1.53 and 0.84 pounds of protein, respectively, while 1.20 and 0.60 are the respective amounts contained in the corresponding parts of the high-protein corn.

If we add together the horny parts and then add together the crown starch and tip starch, as is done in the practical selection of seed corn by mechanical examination, we obtain the results shown in Table V.

TABLE V.—POUNDS OF PROTEIN IN 100 POUNDS OF CORN.

Name of parts.	Low-protein corn.	Medium-protein corn.	High-protein corn.
In tip caps	0.09	0.13	0.08
In hulls	0.27	0.23	0.23
In horny part.....	5.25	6.69	8.20
In white starch	2.37	2.00	1.80
In germs.....	1.91	2.28	2.33
Total.....	9.89	11.33	12.64

It will be observed that the increase in protein in high-protein corn over that in low-protein corn occurs almost entirely in the horny part of the corn kernel. There is also a slight increase in protein in the germ, although this is quite insignificant as compared with the increase in the horny part. In passing from low-protein corn to high-protein corn, there is an appreciable decrease in the amount of protein contained in the white starch. Of course, this is due to the marked decrease in the actual amount of white starch in high-protein corn. Indeed, this decrease in the quantity of white starch is even more marked than would appear from Table V, because the white starch in the high-protein corn is actually richer in protein than that in low-protein corn, as would be expected and as is shown in Table I.

The data given in Table V strongly confirm the results which we have already obtained in practical experience in corn-breeding. For example, we have been breeding both high-protein corn and low-protein corn for the past seven years. In the high-protein corn we find that the proportion of horny part has increased very markedly, while the white starchy part has markedly decreased. In the low-protein corn the opposite is true, the horny part having decreased and the white starchy part having markedly increased, in proportion.

By computation from the data given in Table IV, we have constructed Table VI, which shows the percentage distribution of the different chemical constituents among the several physical parts of the corn kernel.

TABLE VI.—PERCENTAGE DISTRIBUTION OF CHEMICAL CONSTITUENTS AMONG PHYSICAL PARTS.

Ear No. 1 (low in protein).

Name of parts.	Per cent. of total protein.	Per cent. of total oil.	Per cent. of total ash.	Per cent. of total carbo- hydrates.
In tip caps.....	0.89	0.33	0.81	1.29
In hull	2.75	1.21	3.34	6.03
In horny gluten.....	22.56	11.13	7.96	10.41
In horny starch.....	30.51	1.43	4.98	40.22
In crown starch.....	15.52	0.97	5.07	23.18
In tip starch	8.46	0.95	2.96	15.12
In germs.....	19.31	83.99	74.87	3.75
Total	100.00	100.01	99.99	100.00

Ear No. 2 (medium in protein).

In tip caps.....	1.14	0.69	1.06	1.56
In hull	2.07	1.03	3.06	6.80
In horny gluten.....	16.67	12.21	9.56	7.15
In horny starch.....	42.36	2.32	7.38	51.12
In crown starch.....	11.88	0.59	2.67	8.96
In tip starch	5.75	0.68	1.72	9.45
In germs.....	20.14	82.43	74.55	4.97
Total	100.01	100.00	100.00	100.01

Ear No. 3 (high in protein).

In tip caps.....	0.59	0.65	1.76	1.84
In hull	1.85	0.93	3.90	7.12
In horny gluten.....	25.88	12.29	13.49	11.41
In horny starch	39.00	1.98	5.49	49.31
In crown starch.....	9.45	1.44	2.99	15.58
In tip starch	4.77	2.25	2.89	9.32
In germs	18.45	80.46	69.46	5.43
Total.....	99.99	100.00	99.98	100.01

It will be seen that as an average about 22 per cent. of the total protein is contained in the horny gluten, nearly 40 per cent. in the horny starch, and nearly 20 per cent. in the germ; thus these three parts contain about 80 per cent. of the total protein in the kernel.

The germ contains from 80 to 84 per cent. of the oil, while all other parts combined contain only 15 to 20 per cent. of the total oil in the kernel. Based upon this fact is the method for selecting high-oil or low-oil seed corn by mechanical examination, the ears whose kernels show a large proportion of germ being high-

oil corn and those with small germs, low-oil corn. About 12 per cent. of the total oil is contained in the aleurone layer, leaving only about 5 per cent. of the oil distributed among the remaining five physical parts, and, as stated above, more or less of this small amount is undoubtedly absorbed from the contiguous germ or aleurone layer. It will be noted that the ash is closely associated with the oil, nearly 75 per cent. of the total ash being contained in the germ, and about 10 per cent. in the aleurone layer as an average.

Table VII shows, for direct comparison, the percentage distribution of the protein among the different physical parts, in each ear, the two horny parts, and also the two white starchy parts, being combined as in Table V.

TABLE VII.—DISTRIBUTION OF 100 GRAMS (OR 100 POUNDS) OF PROTEIN AMONG THE PHYSICAL PARTS AS OBSERVED IN MECHANICAL EXAMINATION.

Names of parts.	Low-protein corn.	Medium-protein corn.	High-protein corn.
In tip caps	0.89	1.14	0.59
In hulls	2.75	2.07	1.85
In horny part,	53.07	59.03	64.88
In white starch	23.98	17.63	14.22
In germs	19.31	20.14	18.45
Total	100.00	100.01	99.99

Table VII illustrates very plainly the fact that, as we pass from low-protein corn to high-protein corn, the protein decreases in the white starchy part and increases in the horny part; in other words in breeding corn for high protein, we decrease the white starchy part, which is comparatively poor in protein, and increase the horny part, which averages very much richer in protein, the horny starch containing 2 to 3 per cent. more protein than the white starch, and the horny gluten (aleurone layer) being richer in protein than any other part of the kernel. As a rule, in breeding for high protein there is also a slight increase in the proportion of germ, which, being rich in protein, adds somewhat to the increase in protein.

**CRITICAL REVIEW OF THE SECOND SERIES OF ANALYSES
OF MATERIALS FOR THE PORTLAND CEMENT IN-
DUSTRY MADE UNDER THE AUSPICES OF THE
NEW YORK SECTION OF THE SOCIETY
OF CHEMICAL INDUSTRY.**

BY W. F. HILLEBRAND.

Received September 22, 1903.

THE efforts of a committee of the New York Section of the Society of Chemical Industry, headed by Mr. Clifford Richardson, to improve the state of technical analysis in this country are doubtless known to many, if not most readers of this Journal. The subjects thus far taken up have been Portland cement and copper slag analysis, the latter initiated by Mr. Thorn Smith, of Isabella, Tennessee. Carefully prepared samples were sent to many chemists and the tabulated results of analysis were handed over to me for examination and criticism. A report on each subject was rendered. The first, on Portland cement and raw limestone mixture, was published as a part of the Committee's report in the *Journal of the Society of Chemical Industry*, January 15, 1902.¹ In the number of October 15, 1902, there is a criticism of it by Messrs. Stanger and Blount, with attendant discussion by others. The report on copper slag analyses has not appeared in print, but in the *Engineering and Mining Journal*, 75, 295, the list of analyses is given with extended comments by Mr. Thorn Smith, based upon this report, of which copies had been sent to the gentlemen who had made the analyses. Following the first cement report, which contained a tentative scheme for technical analysis by the committee, a second series of samples was distributed for analysis in accordance with its directions. Upon the data thus secured, a second report was rendered by me to Mr. Richardson, and at his request I have prepared, for publication, the present paper, which contains the greater part of that report in practically its original form. In preparing the report, much chemical work was done in the laboratory of the United States Geological Survey, the results of which were tabulated and discussed, but, however interesting they may be from some points of view, they are not all of sufficient importance to warrant the consumption of space required for their presentation herein.

¹ This Journal, 23, R 289.

A cursory glance over the tabulated results of the present series of analyses offers little encouragement to those who hoped for a decided improvement over the first series made in 1901. But it requires no very critical examination to show that there is improvement in certain directions and that the outlook is not all dark. It is unfortunate for the purposes of a satisfactory review of the data presented that the committee's provisional scheme of analysis allowed any discretion as to whether certain corrections throughout the analysis should be made or not; for instance, the correction of silica by hydrofluoric and sulphuric acids, of alumina by potassium acid sulphate, and in the matter of double precipitation of alumina, lime, and magnesia. Thus, while nearly all the chemists practiced double evaporation and filtration for silica and almost all of these blasted silica, but thirteen applied the hydrofluoric acid correction; fifteen precipitated lime twice, but only eleven took the same precaution with magnesia. It would have been more satisfactory had the samples been sent only to those having adequate facilities and agreeing to faithfully carry out the analyses according to a strictly laid down procedure, from which no important deviation could be allowed. Then, and then only, could the results be thoroughly comparable and admit of plain deductions. As it is, so few have adhered throughout to the committee's recommendations that the task of sifting the data has been very arduous and the results by no means commensurate with the labor expended.

This last statement is strengthened by the fact, revealed by special inquiries during the last stages of the examination, that the water used by a number of chemists was so impure as to vitiate their analyses as to certain constituents. Only a few gave quantitative data on the quality of the water used by them, although information on this point was requested of all, but from the replies received it is manifest that not a few of the poor results are directly attributable to this cause and that the quality of the water used is often shamefully bad. One chemist, in fact, declined to undertake the analyses at all because of the poor quality of the only water that was at his service. Another analyst (2), after sending in his report and finding that his water yielded, on evaporation, 16.7 mg. per liter of residue—chiefly magnesium chloride and sulphate—repeated his analysis in duplicate with pure water and reported the results under 2a, Tables II

There is shown a total gain during two months of but 0.75 per cent. when nearly fully exposed to the air. Even though this gain took place almost wholly early in the time period, it is not probable that in the closed vessel an appreciable increase of weight occurred. This conclusion is important, for, if true, it excludes as a probable source of serious error in this series of analyses that due to unequal absorption of carbon dioxide and water by the different samples of cement analyzed. It will be remembered that in the first series of analyses this was held to be a not improbable cause of the wide differences in "ignition loss" on the cement, an opinion which has lost most of its force, in view of the experiment referred to later under *Ignition Loss* (p. 1198).

The analyses made as standards of comparison head the lists given below. Their values are usually the mean of several closely agreeing determinations for which not quite the same degree of accuracy is claimed as for those made in 1901. In addition, others were made to test the committee's analytical scheme and the effect of using glass and porcelain vessels. From the first it appears that the committee's scheme is well adapted to furnish results that afford entirely satisfactory agreement with the standard, a conclusion which is confirmed by the concurrent testimony of several of the analysts who participated in the first series and who have since reported to the committee their experience with the method.

In this connection it may be as well to note that in my subsequent discussion I shall take into consideration some of the criticisms offered by Messrs. Stanger and Blount in their paper already referred to, and to which I, in part, replied at the time of its presentation in New York. A few of the criticisms and suggestions are, in my opinion, valid and good, and may well be heeded, should it seem fit in the light of experience to modify the committee's analytical procedure. Here it is incumbent upon me to point out that Mr. Blount and a number of others have fallen into error in thinking that the committee's method was devised by myself. Although it was submitted to me for comment and criticism and most of my suggestions were adopted, others were not. I purposely refrained from assuming the responsibility of devising a procedure to be followed by a class of factory chemists with whose laboratory facilities and general environment I had

no acquaintance. The scheme having been submitted to me for criticism, I made certain suggestions on what seemed to me the line of improvement from the chemical side chiefly, and there my responsibility ends. This is not to say that in my estimation the procedure is incapable of affording exact results when carefully followed (pure water and chemicals being assumed), for the contrary has been proved by myself and others. It was, however, admittedly a tentative scheme of analysis, open to and probably susceptible of betterment, in the matter of time at least. Mr. Blount has done us all a service in pointing out, in part, the way thereto. In the proper place I, too, shall indicate wherein modifications may, with advantage, be made both in view of certain suggestions of Mr. Blount and as a result of numerous experiments by myself on the slurry and cement samples now under discussion.

The standard analyses were made in general accordance with the outline of procedure given by me in my first report of 1901, but without regard to most of the minor constituents, except to ascertain that they were not present in such amounts that neglect to determine them would introduce errors of importance. Phosphorus and titanium are both present, but are counted in the analysis as alumina. No distinction is made between the different conditions of iron, but all is given as ferric oxide. Manganese is present, but in amount not to exceed 0.05 per cent. Its effect on the lime and magnesia figures has been ignored. Sulphur exists in both slurry and cement as sulphate and sulphide, the latter passing by ignition into sulphate without any loss at all, if the heat is not too prolonged or too high. This last subject is discussed further on in connection with the ignition loss (p. 1198). The alkali percentages are given because these constituents have an important bearing in explaining some of the variations for "loss on ignition," as will appear later (p. 1200).

The slurry was converted, in not over fifteen minutes, by a good blast, into a cement yielding but 0.05 per cent. of matter insoluble in hydrochloric acid. The contrary experience of some of the analysts is due solely to an ineffective blast or an improper manner of applying it, as with the crucible uncovered. The cement, when briefly treated with hydrochloric acid, yielded only 0.09 per cent. of insoluble matter after freeing from some separated silica, which amount might have been lessened perhaps by longer

action of the acid. These slight amounts of insoluble matter from both slurry and cement have not been entered separately, but were weighed with the silica, and what may have been left of them after correction by hydrofluoric acid was carried over to the alumina and iron. The error due to the possible presence in them of lime or magnesia is very slight indeed.

TABLE I.—STANDARD ANALYSES OF SLURRY AND CEMENT.

SO ₃	1.43	} 1.82 SO ₃ ¹	1.53	} 1.75 SO ₃
S	0.16		0.09	
SiO ₂	13.51	} 4.93	21.93	} 8.34
Al ₂ O ₃	3.50		5.99	
Fe ₂ O ₃	1.43		2.35	
CaO	40.84		62.92	
MgO	0.75		1.10	
K ₂ O	0.79		0.61	
Na ₂ O	0.22		0.29	
H ₂ O	4.20		1.40	
CO ₂		1.73	
Ignition		2.91 ⁴	

TABLE II.—ANALYSES OF SLURRY.

Standard.	SiO ₂ 13.81.	Al ₂ O ₃ Fe ₂ O ₃ 4.93.	Al ₂ O ₃ 3.80.	Fe ₂ O ₃ 1.43.	CaO. 40.84.	MgO. 0.78.	SO ₃ 1.43.	Ignition loss. 37.50.
1	(12.69)	(7.07)	(40.46)	(0.72)	36.36*
2	(13.24)	(5.36)	(3.51)	(1.85)	(41.06)	(1.25)	(1.62)	39.62†
2a	(13.46)	5.00	3.77	1.23	40.90	0.79	1.42	37.46
	(13.54)	4.98	3.75	1.23	40.80	0.73	37.46
3	13.95	4.97	3.01	1.96	40.95	0.81	38.66
4a	13.78	4.94	3.28	1.66	41.42	0.62	38.84
4b	13.80	4.84	41.48	0.88	38.90
5	12.62	5.32	4.07	1.25	40.96	0.92	38.88
6	(12.96)	5.30	41.04	0.65	39.68
7	(15.00)	(4.61)	(2.58)	(2.03)	(42.13)	(1.25)	1.62	38.58
8	(15.54)	(4.90)	(3.76)	(1.14)	(42.27)	(1.50)	1.52	39.20
9	(12.76)	(5.51)	(4.13)	1.30	41.98	0.77	1.48†	38.90
10a	13.39	5.22	40.96	0.88	...	37.32
10b	13.16	5.31	40.93	0.85
11	13.20	5.98	3.75	2.23	40.21	1.20	1.62	37.69
12	13.72	5.28	3.68	1.60	41.18	0.79
13	12.88	5.02	2.36	2.66	40.50	0.86	...	39.04
14‡	12.10	5.10	41.00	0.90	1.75	37.38
15	13.55	5.02	41.40	0.79
16	12.78	6.22	41.18	1.07	...	37.48
17	14.38	5.14	42.17	0.82	1.43	37.32
18	12.61	5.53	3.77	1.76	41.26	1.33	1.54	37.78
19**	(14.91)	(4.20)	(3.02)	1.18	41.71	1.10	1.48	35.15

¹ By fusion, after slow ignition and subsequent extraction by HCl, there was found the same total—1.82.

² TiO₂, 0.18.

³ TiO₂, 0.31.

⁴ Mean of many results. The calculated loss from H₂O.CO₂ and the difference between 2+8 and Fe₂O₃+8H₂O is 2.99. The slight discrepancy between the calculated and determined values may well be due to errors in the H₂O and CO₂ rather than in the directly found value for loss.

4a. Committee's method. 4b. Analyst's method. 7 and 8. Different analysts at same works. 10a. Committee's method. 10b. Analyst's method. * Average of five determinations. † Including 1.03 SO₃. ‡ Also 0.10 S. § Also 0.77 K₂O and 0.45 Na₂O. ** The figures of 19 are not in the form reported by the analyst, who gave analyses of soluble and insoluble parts separately.

TABLE III.—ANALYSES OF CEMENT.

Standard.	SiO ₂ . 21.93.	Al ₂ O ₃ · Fe ₂ O ₃ . 8.34.	Al ₂ O ₃ . 8.98.	Fe ₂ O ₃ . 2.38.	CaO. 62.92.	MgO. 1.10.	SO ₃ . 1.84.	Ignition. loss. 2.91.
1	22.29	9.68	62.81	0.95	1.52*	2.37†
2	(22.38)	(9.54)	(6.46)	(3.08)	(62.98)	(1.60)	(1.73)	2.66
2a	{ 22.08	8.44	6.18	2.26	62.90	1.11	1.54
	{ 22.04	8.50	6.20	2.30	62.80	1.15
3	22.10	8.72	5.78	2.94	63.44	1.23	1.52	2.71
4a	21.70	8.60	6.06	2.54	63.56	1.37	1.51	2.84
4b	21.68	8.46	63.56	1.25	1.52	2.85
5	21.20	9.04	6.67	2.37	63.13	1.39	1.58	3.48
6	22.08	8.66	63.09	1.31	1.63	3.74
7	(22.86)	(9.21)	(6.15)	(3.06)	(63.96)	(2.82)	1.56
8	(22.02)	(9.25)	(6.64)	(2.61)	(64.43)	(2.62)	1.38
9	21.69	8.64	6.19	2.45	63.27	1.08	1.43‡	4.50
10a	21.86	8.83	6.35	2.48	63.49	1.19	1.59	2.96
10b	{ 21.79	8.83	6.35	2.48	63.40	1.20
	{ 21.71	8.89	6.36	2.53	63.40	1.21
11	22.27	8.83	6.24	2.59	62.53	1.21	1.57	3.30
12	22.32	8.64	6.19	2.45	63.40	1.64	1.55
13	21.88	9.18	4.88	4.30	63.01	1.38	1.61§	2.66
14**	20.50	8.41	62.60	1.20	2.26	4.20
15	22.44	8.62	62.14	1.02	1.55	2.32
16††	22.18	8.52	63.88	1.28	2.86
17	22.24	8.36	63.72	0.99	1.46	3.01
18	22.58	9.08	6.48	2.60	63.15	1.36	1.51	2.58
19	22.53‡	8.39	5.74	2.65	63.88	1.34	1.62	0.98

4a. Committee's method. 4b. Analyst's method. 7 and 8. Different analysts at same works. 10a. Committee's method. 10b. Analyst's method. * Also 0.06 S. † Mean of two concordant results. ‡ Also 0.10 S. § Also 0.19 S. ** Also 0.85 K₂O and 0.50 Na₂O. †† Mean of close duplicates. ‡‡ In addition 0.20 insoluble in HCl reported.

Examination of the data furnished by most of the chemists with their analyses shows that certain of the latter must be rejected, in part at least, as not made in accordance with the committee's specifications in essential details. Slight deviations which could hardly affect the results appreciably, if at all, have not been regarded as sufficient ground for exclusion. This rule affects certain of the slurry analyses, and the values which are

regarded as fitly thrown out appear bracketed in the accompanying tables. With fuller information it is likely that still other figures would be similarly treated.

The grounds for excluding from discussion the bracketed values are the following:

Nos. 1 and 16.—The chemists, being unable to secure complete conversion to a soluble state by ignition, treated the partially converted slurry with hydrochloric acid, and, instead of filtering and further handling the residue as directed by the committee, evaporated silica and insoluble as for silica alone and corrected by hydrofluoric and sulphuric acids. No. 1 then found, after ignition, a fixed residue of 2.37 per cent., and No. 16 one of 2.60 per cent., which was, in each case, deducted from the crude silica and added to the alumina and ferric oxide obtained by precipitation with ammonia. Hereby a serious error was committed, affecting not only the value for silica, but those for alumina, lime, and perhaps magnesia as well, for the residue consisted not simply of aluminum and iron oxides, but of a little magnesia and probably considerable calcium sulphate too. The silica is thus made to appear too low by the amount of SO_3 retained by the lime, for, in case of No. 1, at least, the blast temperature was insufficiently high to convert to oxide. The lime and magnesia are also too low, but the alumina too high by the extent of the calcium sulphate and magnesia in the residue from the silica. In this way the quite abnormally high values for alumina and ferric oxide can be, in part at least, accounted for, but it is singular that analyst No. 1 should be the one to report also the highest alumina and ferric iron in the cement, where the conditions were normal and his silica and lime are nearly correct.

No. 2.—This analyst, after reporting, found that his water carried 16.7 mg. of solid matter to the liter, in large part chloride and sulphate of magnesium. His silica and lime values, particularly the latter, do not seem to be materially affected by the impurity of the water, but it has been thought best to reject the entire analyses for both slurry and cement. The analyses under 2a are the work of the same analyst when using pure water, but as they were made after seeing the standard analyses, it is not right to consider them in the discussion.

No. 6.—In this case the insoluble and silica were fused with sodium carbonate, but instead of adding the hydrochloric acid solution of this fusion to the original filtrate it was separately evaporated twice for silica, the first filtrate also, whereby a greater loss of silica was incurred than if the combined solutions had been treated together.

Nos. 7 and 8.—These chemists, attached to the same works, did not ignite the slurry, but dissolved directly in acid and fused the residue with alkali carbonate. Under ordinary circumstances this procedure should not have caused trouble, but the slurry contained considerable organic matter, soluble in acid, which may have affected the subsequent precipitation of iron and aluminum to a marked degree. It is quite impossible to account in this way for the extraordinary values reported for silica, or for the excessive percentages for lime and magnesia, which characterize both slurry and cement analyses by these chemists, and for alumina in their cement analyses. Especially impossible are the figures given for magnesia in the cement. The fact also that two chemists following the same procedure should be able to find 1.14 and 2.03 per cent. of Fe_2O_3 , respectively, speaks for itself. Either the grossest incompetence marks these analyses or the reagents used were of phenomenally bad quality. The glassware can hardly be more at fault than in the other analyses, for it is asserted to be Bohemian and furnished by a well-known New York firm. The analyses are therefore excluded, not only in the case of the slurry but of the cement also, as unworthy of serious discussion.

No. 9.—Portions of this analysis are rejected for the same reason as 7 and 8, that is, the manner of effecting solution of the slurry. The iron determination, being made on a separate portion and possibly after solution in a different manner, is not excluded. The cement analysis of this chemist shows normal character, notwithstanding certain deviations from the committee's rules.

No. 19.—The residue from incomplete conversion of the slurry to a soluble state by ignition was fused with sodium carbonate and analyzed separately, not being united with the first filtrate. This introduced uncertainties in the subsequent determinations, the reality of which is sufficiently apparent from a comparison of the values for silica and alumina with those of the standard, and hence justifies exclusion in part.

In individual determinations, a few of the other analyses show lapses from proper care quite comparable with those of 7 and 8, as, for instance, the silica values of 14 and the iron values of 13 in both slurry and cement, and of 11 in the slurry, but the data afforded by the chemists as to the methods used and the internal evidence of the analyses themselves do not furnish sufficient grounds for exclusion wholly or even in great part. Wide variations of the alumina values from the standard are not taken account of when it is plain that this is the result of an erroneous iron determination.

Were space available, it would be of interest before discussing the foregoing analyses to reproduce certain tables and attendant comments of the full report, showing the results obtained by myself when closely following the committee's procedure (using platinum vessels), and also the effect of completing the analyses, after separation of silica, in glassware of different makes. The tables referred to also show not only the percentages derived from the first crude weights, but also those found by applying the corrections usual in exact analysis. It must suffice to summarize the net results.

(1) That with pure reagents and only ordinarily careful work no such variations should be possible as are shown by Tables II and III, even when glassware of good quality is employed instead of platinum. Analyses of the cement made in glass gave: SiO_2 , 22.08, 22.10, 22.11, 22.02, 22.30, 22.04; Al_2O_3 , Fe_2O_3 , 8.39, 8.43, 8.39, 8.22, 8.41, 8.37; CaO , 63.18, 63.03, 63.01, 63.18, 63.17; MgO , 1.16, 1.21, 1.12.

(2) That the solubility of glassware should not make itself so apparent by an abnormally high magnesia result as might seem to be the case in certain of the analyses of Tables II and III, for in all the analyses of the omitted list silica was in solution—up to 8 mg.—but, in agreement with all my previous experience, it is precipitated but little, if at all, with the magnesium phosphate. It seems, therefore, probable that the very high magnesia results in the other cases may have been due to magnesium salts in the water used, as well as in No. 2.

(3) That with cements so completely soluble in acids as the present one, the correction of the silica by hydrofluoric acid and of the alumina by bisulphate ought to be for technical work, certainly for factory control, unnecessary, since they so nearly bal-

ance one another. Any one of my analyses made in glass would serve quite well for all practical purposes, but unfortunately very few of the analyses in Tables II and III conform throughout to the standard anywhere near so well. There is evidently something wrong with the manipulations or the reagents used by the several chemists, as a consequence of which few are able to secure results as good as the least satisfactory of those in the omitted table. They evidently do not work as I do, and, moreover, they do not work alike among themselves. The personal factor seems to be an important one.

(4) That while it might be safe under the conditions assumed above to neglect the corrections on silica and alumina (as was done by analyst 12), it is not safe to apply one and neglect the other. This the following illustration will make clear: The uncorrected values for SiO_2 and Al_2O_3 were 22.12 and 8.59, which became 22.00 and 8.71 when correction was applied to the former only; but the latter held 0.30 SiO_2 , so that the true values were 22.30 and 8.41. The wholly uncorrected figures were nearer right than when but half corrected.

DETAILED DISCUSSION OF ANALYSES OF TABLES II AND III.

It is now in order to look at the analyses in greater detail, and because the determinations of silica and alumina are so closely connected, I will discuss under one heading the figures given for silica and the precipitate produced by ammonia.

Silica and the Alumina Precipitate.—The cause mentioned just above, namely, the application of the correction on the silica for alumina and not on the alumina for its contaminating silica, accounts for the chief discrepancies in Tables II and III after excluding the "rejected" values enumerated on pages 1188-1189. This is shown by the following tabulations, where Table IVa contains the analyses in which the double correction was made, while IVb shows those in which the correction was made only on the silica. The silica was blasted in all cases.

TABLE IVa.—SHOWING ANALYSES IN WHICH THE CRUDE SILICA AND ALUMINA WERE BOTH CORRECTED.

No.	Slurry.		Cement.	
	SiO_2	$\text{Al}_2\text{O}_3\text{Fe}_2\text{O}_3$	SiO_2	$\text{Al}_2\text{O}_3\text{Fe}_2\text{O}_3$
3	13.95 ¹	4.97	22.10	8.72
4a	13.78	4.94	21.70	8.60
10a	13.39	5.22	21.86	8.83
11	13.20	5.98	22.27	8.83
17	13.38	5.14	22.24	8.36

¹ No hydrofluoric acid correction.

TABLE IVb.—SHOWING ANALYSES IN WHICH CRUDE SILICA BUT NOT THE CRUDE ALUMINA WAS CORRECTED.

No.	Slurry.		Cement.	
	SiO ₂ .	Al ₂ O ₃ Fe ₂ O ₃ .	SiO ₂ .	Al ₂ O ₃ Fe ₂ O ₃ .
1	22.29	9.68
5	12.62	5.32	21.20	9.04
13	12.88 ¹	5.02	21.88	9.18
14	12.10	5.10	20.50	8.41
15	13.55 ²	5.02	22.44 ²	8.62
16	22.18 ¹	8.52
18	12.61	5.53	22.58	9.08

In the first of the above tables, the four silica values for slurry, due to double correction, all fall within the limits 13.20 and 13.78, the standard being 13.51. Analysis 3 is included in this series, notwithstanding the omission of the hydrofluoric acid correction, because it is plain that with the correction made it would occupy an even more favorable place than it does with respect to silica.

The second table contains four of the eight markedly low silica results reported for the slurry— that is, below 13 per cent.— while only one is above 13 per cent. In this, the evaporation for silica was made in glass, while in the other cases porcelain was used, except platinum for the slurry in 13. The other four returns below 13 per cent., namely 1, 6, 9 and 16, are excluded from consideration for the reasons given on pages 1188-1189.

With respect to the silica values for the slurry in Table IVb, it seems singular that with such a low general average of uncorrected alumina for the five, the silica should not be much higher than it is. Assuming that the alumina is all accounted for in the values given, there must have been a marked loss of silica in four of the five analyses. Were the alumina considerably higher, the same cause might be assigned that was sufficient to exclude slurries Nos. 1 and 16 from the comparisons, but there is nothing in the data furnished by the chemists who made these analyses that throws any light upon this point. Were it not for the fact that similar deficiencies do not appear in their cement analyses, it might be thought that in some of the cases silica had adhered so tenaciously to the porcelain dish on evaporation as to escape complete removal. This is a cause of error quite likely to arise at times when using porcelain, because of the difficulty of seeing the adhering silica against the white surface. Analyst 16, who evaporated for silica twice in platinum, remarks that the glass

¹ In platinum.² In glass.

used for subsequent operations was "easily attacked," which might account, in part, for his abnormal alumina in the slurry, were it not that for the cement it is nearly normal.

Notwithstanding that the results of Table IV^a are, on the whole, most emphatically favorable to the application of the double correction, the fact remains that the general average of the alumina is still far in excess of the standard. This may be in part because the silica correction, as made by bisulphate, does not give the true correction, as I showed conclusively in my paper "Common Errors in the Determination of Silica,"¹ since a large, or even a major, portion of the silica contaminating the alumina goes into solution and can only be recovered by evaporating the dissolved product of fusion with excess of sulphuric acid, and heating till fumes of the acid are copiously evolved. Upon cooling, diluting, and digesting for a time, the whole of the silica collects in flocks and can be readily separated and determined. See, also, page 1205.

In all cases where alumina was twice precipitated (and this was done by all but 3 and 15), except under the conditions of treating the slurry followed by analyst 1, there is no reason to suppose that the high results for alumina are due to coprecipitation of calcium, even when the ammonia used contained carbonate and the liquid, during precipitation, was exposed to gases from the flame beneath. Therefore the variations in the lime and magnesia must be due, in the great majority of cases, to causes quite unconnected with the manner of getting the slurry and cement into solution and with the determining of the silica and alumina, except in the case of slurry No. 1, already alluded to, and possibly one or two others. This it would be impossible to assume, had but a single precipitation of alumina been made, for most chemists do find a little lime with the latter when they take the trouble to look for it, although of the present company 3 and 15, the only ones who tried it, seem to have made a good single separation, as Mr. Blount claims can always be done by the use of a sufficient amount of ammonium chloride. I must admit that a single trial, by myself, on the cement gave a result in accord with his statement, but then I use redistilled ammonia, which is almost free from carbonate, while that coming from the dealers contains a good deal at times and may thereby give rise to rather serious error.

¹ This Journal, 24, 36a.

The excessive value obtained by No. 1 for $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ in the slurry has been shown to be due, in part, to the possible counting of considerable calcium sulphate and a little magnesia as alumina, but since an almost equal excess occurs in his cement analysis without the possibility of a similar cause acting, the explanation must lie, in part, in the application of too low a heat. If the alumina was heated with uncovered crucible, as seems to be this chemist's practice, the error may be accounted for.

To sum up the situation as regards silica by a review of all the data, regardless of just grounds for excluding some, it appears that there has been a decided elevation in the average. It is nearly that of the standard in the slurry (13.43:13.51) as against 14.37 to 15.18 of the 1901 series, showing an average deficiency of only 0.08 per cent. now, as against 0.81 then. In the cement there appears now an average excess of 0.10 per cent. (22.03:21.93), as against a deficiency of 0.81 in 1901 (20.50:21.31). It is thus apparent that, whereas two years ago the average error of a large number of chemists was a serious minus one, it is now, in both cases, practically wiped out. The variations from the truth are as likely to be found on one side as the other, though the extremes are as far apart as ever. This last would be a more discouraging feature than it is but for the fact that the returns from analyses 7, 8, 9, 14 and 19 are so abnormal on the slurry as to occupy a position by themselves. Excluding their results, the extreme differences show a marked improvement also, being for the slurry only 1.34 now, as against 2.97 in 1901, and for the cement (excluding here only 14 as utterly abnormal) 1.18 against 2.38.

A similar comparison of the precipitates by ammonia shows the following results: The general average for the slurry is now 0.35 in excess of the standard (5.28:4.93) as against an excess of 0.84 in 1901 (7.93:7.09), and for the cement 0.52 in excess (8.86:8.34) as against 0.90 (10.33:9.43) in 1901. The real showing is doubtless somewhat less favorable than it appears from the above, because the alumina precipitates are now smaller than in the earlier series of analyses, but there is nevertheless a manifest improvement.

Iron.—In the foregoing the ammonia precipitate has, for brevity's sake, been spoken of as alumina. The values for the latter constituent, being in all cases determined by difference, are,

of course, affected by any error attaching to the iron. As stated earlier, gross carelessness must have characterized some of the iron determinations. The gravimetric determinations (3 and 19), after separation from alumina by potassium hydroxide, were wide of the standard, as may be seen by reference to Tables II and III, but not to the same degree as some of those made volumetrically. It is of interest to know that the hydrogen sulphide method of reducing iron has given decidedly better results than reduction by hydrogen, though there is still room for improvement by those using the former method.

Aside from carelessness in one way or another, it seems probable that a not unimportant factor in some of the errors is the strength of volumetric solution used. In most cases it was too strong for safety in rapid work on low iron percentages, being from 0.0055 to 0.0105 Fe per cubic centimeter.

Lime.—Except as before mentioned for slurries 1 and 16, the determinations of lime seem to be unaffected by any of the variations from the committee's directions for the solution of the slurry and cement, and there are no data to throw light on the cause of the wide variations, not only from the standard, but among themselves as well. The errors due to solvent action on the glass beakers should affect chiefly the silica and lime, and a portion of all the plus errors in these determinations are to be ascribed to this source. But, as my own analyses made in glass go to show, the errors resulting herefrom are not great enough to account for the large variations reported, unless the glass is much poorer than any that was at my disposal. Neither does there seem to be any decided advantage in the gravimetric method for lime over the volumetric one involving the use of permanganate, except in the case of the cement, where the maximum difference is 1.35 in eleven determinations as CaO against 2.29 by permanganate. If, however, the grossly inaccurate analyses of 7 and 8 are excluded from consideration here as before, the advantage is found to lie slightly with the volumetric method for both slurry and cement, leaving out of account the discrepancy in numbers.

There is internal evidence in a few of the analyses that insufficient heat was employed to convert the oxalate wholly to oxide. For instance, 17 shows in all respects, except lime, a close agree-

ment with the standard, whereas in lime his results are far above the average on both slurry and cement. The last statement holds for 19 too, though the agreement with the standard is not otherwise good. No. 11, on the other hand, shows a marked loss in both cases, with especially high alumina in the slurry, which seems to be indicative of incomplete separation from the latter, notwithstanding that the separation was made twice.

With respect to the temperature required for the complete conversion of calcium oxalate to oxide, it will be well to introduce here a few remarks and an experiment to dispel the common impression that this is a difficult matter. Analyst 1 blasts for an hour or more, but when it is learned that this is done with crucible uncovered, the reason is apparent, especially if the blast is not a powerful one. The following test, made by myself, shows what may be accomplished over a good Bunsen burner only.

A crucible containing 2.9997 grams precipitated CaCO_3 , weighed 24.4033 grams. The covered crucible was heated for several periods with the results that follow:

	Grams.
Weight after twenty minutes over burner	23.1628
Weight after further twenty minutes over burner	23.0817
Weight after further twenty minutes over burner	23.0801
Weight after inclined blast for twenty minutes	23.0790

The total loss was 44.12 per cent., instead of the 43.95 called for by theory, the slight excess being doubtless ascribable to hygroscopic moisture. It is seen that forty minutes' heating over the burner sufficed to effect almost the whole of this with 3 grams of calcium carbonate. For the amounts usually encountered in analysis, of which cements afford about the maximum, ten minutes' heat of the Bunsen burner is almost as effective as an additional five minutes' blasting, which latter is usually ample. Could the Bunsen heat be applied effectively with exclusion of the flame gases from the interior of the crucible, the blast would be quite unnecessary at the end. It is, however, assumed that the crucible rests in a triangle of platinum and not of clay. It is also my custom to use an inclined blast on almost all occasions requiring this mode of heat application, and usually without allowing the flame to envelop the lid of the crucible. Hereby flame gases are largely or altogether excluded, and, consequently, in the case of

cements and limestones, given an equal temperature, more rapid loss of their carbon dioxide results than is possible with a vertical blast.

One possible cause of error in the lime results remains to be mentioned. Unless the lime is weighed soon after ignition—say not later than half an hour—the result may be too high. It is not known to what extent, if at all, this error affects the results under discussion.

Magnesia.—Regarding the discrepancies in magnesia there is little that can be said. When averages for 1901 and 1902 are compared, the present are found to be even a little worse than the earlier ones, and that too with smaller amounts of magnesia to deal with. Even allowing for considerable solvent action of reagents on the glass, it is difficult to see how this should give rise to such extraordinary results as some analysts report. It seems not impossible that the abnormally high magnesia returns were, in all cases, due to impure water, as was found to be the case with those of analyst 2. Even where the ammonium salts have been removed by nitric acid (method of J. Lawrence Smith), as recommended by Mr. Blount, the results are still high, as in both analyses 19.

The influence of impurities in stock solutions is one that should not be lost sight of. The practice of using stock solutions of such reagents as ammonium oxalate and sodium phosphate is dangerous, unless the solutions are renewed at frequent intervals. It is my practice to use the solid salt and dissolve it as wanted.

Sulphur.—For all but No. 3, the figures for sulphur trioxide represent only the sulphate sulphur. No. 3 reports only total sulphur. The only point calling for special comment is the comparison of the results as they were obtained with or without removal of silica by evaporation before adding barium chloride. Even excluding the particularly abnormal results of 14, the advantage is still with those who do not remove silica (5, 6, 9, 10a, 12, 17), although the comparison is not altogether satisfactory, because of the difference in the numbers using the two procedures. I am inclined to ascribe the higher values in the one case largely to absorption of sulphuric acid during evaporation for removal of silica, especially where water-baths heated by gas were used. That this source of error is a very real one has been long since shown. Impure water may be a factor in other cases for the

deviations in excess of the standard recorded by both procedures. The high value reported by No. 2, in his original analysis, is known to have its origin in the above source, and it may very well be, in view of the poor quality of the water reported subsequently by others, that this explanation fits other cases. That Stoddart should have found¹ frequently more sulphur in coals when not separating silica than when doing so, is contrary to all my experience in silicate work, where duplicates agree usually exactly, and, if they differ, are as likely to be high by one way as by the other.

Ignition Loss.—The results for loss on ignition will not be discussed in detail because the experiments, referred to below, have shown clearly enough why the results vary, and must vary, unless a closely defined method for determining this loss is followed. Such precision is not to be found in the committee's directions for the determination of this factor; hence, no blame can attach to those who obtain results varying from the standard. Several of the chemists stated that in their results "loss on ignition" comprised not only water and carbon dioxide, but also more or less sulphur trioxide, depending on the temperature of the blast, besides organic matter and possibly one or two minor factors. In my own analyses, it was supposed to include all possible factors except loss of sulphur from either sulphates or sulphides, for, unless the heat passes a certain point, the sulphides are oxidized to sulphates and no sulphur is lost, being retained by the lime. This is the explanation asked for by Mr. Blount in his reply² to certain remarks of mine at the foot of page 1221.

Mr. Blount is perfectly justified in objecting to the blast for "loss on ignition" in cements and cement mixtures containing sulphur when applied in the manner prescribed by the committee, but, as described below, the method is accurate for all reasonable demands, and results agreeing within 0.1 or 0.2 per cent. can be obtained almost as often as desired. It happened that, without special study of the subject, I had employed the right conditions from the start, but Mr. Blount's inquiry led me to take up the matter in some detail, and the results I now communicate.

It may be said at once that the variations in "loss" are not attributable to absorption of carbon dioxide and water from the air, unless there was great lack of care, and even then this can be

¹ This Journal, 24, 852.

² J. Soc. Chem. Ind., 21, 1223.

but a minor cause, as the data given on page 1183 show. Hence, my own former doubts and those of S. F. Peckham¹ on this point were largely unfounded.

Trials in great number were made on both slurry and cement under varying conditions. It was found, as above said, that the sulphides could be easily and quickly oxidized without any loss of sulphur and yet with complete removal of water, carbon dioxide, and organic matter. The proof of this was repeatedly obtained by finding in the ignited product as sulphate soluble in hydrochloric acid exactly all the sulphur that the cement or mixture originally held in both sulphate and sulphide condition. Such a complete change can be effected in a short time and without any need to be very cautious in applying the heat. It may be turned on nearly full at the start.

In all my experiments, ignitions were effected in covered platinum crucibles of about 20 grams weight. Chemist No. 1 followed the practice recommended by me of fitting the crucible in a hole in asbestos board, but removed the cover, and in this last fact lies the explanation of the excessive time required by him for securing constant weight, and the too low results when obtained. My experiments show that even without the protection afforded by the asbestos board there need be no great error with an inclined blast if only the precaution is taken not to let the flame envelop the whole crucible, but only to impinge strongly against the lower third. In using asbestos board, particles tend to cling to the crucible and to remain attached when the latter is removed after ignition; hence, I prefer, as much cleaner and no more expensive in the end (for the same asbestos serves but a few times), a sheet-platinum disk with a hole for the crucible, the disk in its turn covering a larger hole in asbestos board. A further advantage of this modification is that, because of the higher heat obtained than when the crucible is in contact with asbestos, the duration of the heating is shortened. A muffle answers equally well, as claimed by Mr. Blount (for time required see page 1207).

I have assumed that the loss shown when none of the sulphur has as yet been expelled is to be taken as correct, since in no case was there the slightest effervescence on dissolving in hydrochloric acid, nor any trace of organic matter left. That this assumption is entirely justified was shown by the close agreement

¹ *J. Soc. Chem. Ind.*, 21, 831.

(in case of the cement, for which alone could the calculation be made) of this value with that obtained as the algebraic sum of all factors entering into the loss. A similar agreement appeared in my discussion of the 1901 series of analyses. But, because of the unavoidable variations in the heat supply used by different chemists, each one should ascertain, once for all, the effectiveness of his burner, blast, or muffle, by ascertaining, as I did, the limit of time beyond which sulphur begins to be volatilized, as shown by the ignited "mix" or cement yielding less total sulphur than before ignition. This necessarily, however, involves rather more accurate determinations of sulphur than most of those reported either now or in 1901.

The temperature at which carbon dioxide escapes from calcium carbonate being so much lower than that causing dissociation of the sulphate, is the reason why comparatively brief application of heat under the above conditions effects complete loss of carbon dioxide and little or none of sulphur trioxide. But it is not the above mode of ignition that must be used to convert the slurry to a wholly soluble cement. No disk protection is then allowable.

It is apparent from my experiments that most chemists employed far too protracted ignition in determining "loss," and that in extreme cases all, or nearly all, the sulphur trioxide was included in the loss. But in many cases there was a further factor making itself felt, for long before the last of the sulphur trioxide is expelled alkali begins to volatilize, and it is easy to remove all, or nearly all, in this manner. The alkali is volatilized as oxide and may be collected in quantity on the under side of the crucible lid. At the intense temperature of the rotary cement furnace this action must play an important part, and to it is to be attributed the great loss of alkali, noted by me in the cement of 1901, as compared with the raw "mix" from which it was made, an observation which is repeated in the present case and must be general in cement burning.

PROPOSED MODIFICATIONS IN THE COMMITTEE'S DIRECTIONS FOR THE
ANALYSIS OF CEMENTS.

From the foregoing it is apparent that the committee's method of procedure has, in many respects, not been subjected to a fair or exhaustive trial. Furthermore, because of the real uncertainty regarding the quality of much of the water used, the value of this

report is below what it would otherwise be. Nevertheless, certain facts have appeared from my experimental work in the light of which modifications of the committee's directions for the analysis of Portland cements and raw mixtures used in their making are in order. These I will now consider.

Rendering Raw Material Soluble.—The committee's direction, following my own recommendation, to ignite the "mix" at an intense heat in order to render it soluble in hydrochloric acid, are thoroughly sound in principle and in accord with the practice of Messrs. Stanger and Blount. By doing this, the material undecomposed by the acid should, in no case, probably, exceed 0.1 per cent. of the sample, and it is sometimes much less. By this it is not meant that no insoluble matter appears other than undecomposed silicates, for a little silica is always separated in a flocculent, non-gelatinous, easily filterable state. The unattacked particles can always be detected by their gritty character when touched with a rod.

Under no circumstances may a large residue of undecomposed matter, found at this stage, be evaporated with the solution to dryness and treated as if it were silica (as two or three chemists have done in the present series of analyses), for it may, and probably does, contain lime in addition to alumina, ferric iron, etc. The error in silica and alumina, caused by this lime being weighed as sulphate, after the hydrofluoric acid correction, has been discussed on page 1188.

The point has been raised that the strongly ignited material dissolves very slowly, being dense and semifused. If, however, the lumps are gently pressed upon with the flattened tip of a rod from the moment the acid strikes them, solution becomes a matter of no difficulty at all. In spite of the ease with which this conversion to a soluble state can be reached in fifteen or twenty minutes, quite a number of chemists failed by lack of blast of sufficient intensity. The committee recommends in such cases to filter off any undissolved matter, to ignite, to fuse it with sodium carbonate, and to add its hydrochloric acid solution to the main filtrate. Had these directions been followed in certain cases, fewer analyses would have been thrown out of court.

In order to obviate the need for a filtration and fusion of a possible residue, one chemist, W. R. Oglesby, recommends to strongly ignite a mixture of the material with only enough sodium

carbonate to cause sintering. It is claimed that solution in hydrochloric acid is then complete, that the amount of alkali introduced is so slight as to give rise to no appreciable error in subsequent operations, and that the necessity for correcting silica by hydrofluoric acid is avoided. My own tests show that the first claim is well grounded when even so little as 0.5 gram of the flux to 1 of "mix" is employed. But the reason for the third is not obvious, for it has never been my fortune to see silica separated by evaporation from a solution containing aluminum, iron, titanium, and phosphorus, or even the first of these alone, which was so pure that no contamination was revealed by the hydrofluoric acid treatment. The residue is rarely under 1 mg. and may be twenty to thirty times that amount in special cases (not cements). My own limited experience with cements shows that it runs from 1 to 2 mg. after a single evaporation for silica and slightly more after a double one. Still, no strong objection can be brought against this method of attack of the raw mixture on the score of accuracy, and if it on a general trial should meet with the approval of cement chemists, there may be no objection to its superseding the blast ignition without addition of flux. But the amount of this flux should be rigidly kept down to the lowest limit, not exceeding that given above.

Determination of Inert Constituents in Cement.—Mr. Oglesby would also apply the above mode of attack to cements as well, but this brings up the question whether the committee shall see fit to take account of the existence of cements containing acid-soluble constituents in appreciable amount. These undoubtedly do exist here, as well as abroad, and it seems reasonable and proper that inert constituents, when present, should be reported as such and not help to swell the active components. But if the determination of these inert constituents is to be made, I cannot recommend that the directions of Messrs. Stanger and Blount be followed, for the reasons set forth in my criticism of certain features of their paper,¹ but must adhere to the procedure there outlined by myself. I do not agree with their statement that no foreign matter is to be found with the silica separated from cements, nor, do I think, will many others do so who look carefully into the matter (see remarks relating to this point a few paragraphs above, page 1201).

¹ *J. Soc. Chem. Ind.*, 21, 1222.

Solution of Cement and Ignited "Mix."—The committee's directions for dissolving cements and ignited cement mixtures may very well be modified in the interest of time-saving by adopting the practice of Messrs. Stanger and Blount,¹ for to digest, and especially to dilute strongly, before evaporating causes quite unnecessary delay. Usually, in two or three minutes after pouring the acid upon the moistened cement, solution is effected and evaporation may begin.

Dehydration of Silica.—Messrs. Stanger and Blount's plan of baking on a hot plate, at a temperature of about 200°, is a very speedy way of rendering nearly all the silica insoluble and saves much time. It may be unhesitatingly recommended for a first evaporation. But at this point my approval of their procedure ceases. I can refer only to my experiments quoted on page 1221² in refutation of the claim that a single evaporation for silica suffices by their procedure. Their later results (p. 1223) only serve to confirm my objections instead of overturning them. If an error of over 0.2 per cent. in the alumina is negligible, then why do the authors regard it necessary to reject, as unfit for use, filter-paper which would introduce into an analysis an error of less than one-tenth of the above? But, in addition, the authors do not give us their way of analyzing the precipitates of Al_2O_3 and Fe_2O_3 in order to show that the amounts of silica they give were all that these precipitates contained. If it were done by solution of the Al_2O_3 and Fe_2O_3 in an alkali bisulphate, they obtained but a minor portion probably of the total silica. As I have shown elsewhere,³ that method, as hitherto carried out, gives utterly fallacious results, and it is only by the exercise of a certain precaution that all silica can be recovered. Even after two evaporations, the iron-alumina precipitate contains usually from 1 to 3 mg. of silica. Nor is this silica "more likely to be due to dust and outside impurities than to residual silica in the cement itself,"⁴ if the water and reagents were pure.

No change should therefore be made in respect to the double evaporation and filtration for silica. It is not important, except

¹ *J. Soc. Chem. Ind.*, 21, 1217.

² *Loc. cit.*

³ *This Journal*, 24, 362.

⁴ *J. Soc. Chem. Ind.*, 21, 1223.

as a matter of time-saving, whether the heating of the separated silica be done at steam-bath temperature or at that of the hot plate.

Alumina, Iron Oxide, Lime, Magnesia.—I do not feel that any fundamental changes in the directions given by the committee for the determination of these constituents are called for either by the comments of different writers or by the testimony of the analyses themselves. The amount of bisulphate to be used for the solution of the ignited alumina, etc., should be reduced from 10 grams to 2 or 3. Care should be taken to make a blank experiment with the reagent to ascertain its silica contents, if it has any.

I agree with Messrs. Stanger and Blount that quite satisfactory separations *can* be made in cements and cement mixtures, of alumina and iron from lime, and of lime from magnesia, by one precipitation, separations which would satisfy all requirements of the cement trade, and I have made them myself. But this can only be accomplished by the employment of really good reagents and utensils. With the ammonia used by nearly every one, varying perhaps in quality originally, not redistilled over lime, and contaminated from the glass bottles, it is hardly possible that accurate results can be obtained by single precipitations. Probably most ammonia used contains carbonate. I have found this to be so with that which we buy as of good quality. Hence, unless carefully redistilled over lime, the aluminum and iron oxides must be contaminated by calcium carbonate. Mr. S. S. Voorhees, of the supervising architect's office of the United States Treasury, finds this contamination to be less than 0.25 per cent., but it may often be more in careless work, and it is to avoid the effect of variable errors like this that I would make double precipitations the rule.

In the numerous analyses made by myself for this report, I have thoroughly tested the time-limit for the settling of calcium oxalate after precipitation, and find that very little, indeed, is gained by allowing to stand for more than twenty minutes after removal from the source of heat. The lime in the first filtrate will hardly ever exceed 1 mg. when the quantities to be precipitated are so great as in limestones and cements.

In blasting lime, the crucible should be always covered, and it is advisable that the blast-flame impinge only against the lower part of the crucible, at an angle of about 45° . The flame should not envelop the lid of the crucible, because when it does the contents are ever in an atmosphere of carbon dioxide, and the complete reduction to oxide is retarded. The heat of a good blast-lamp is, however, so many hundred degrees above the temperature of decomposition of calcium carbonate that no difficulty need be experienced in getting an unchanging weight, even if this precaution is not observed. With it, however, no ignition should ever require over ten minutes, and a second heating is, indeed, rarely made by myself.

I now regard it as quite unnecessary to blast the relatively small amounts of magnesium pyrophosphate obtained in cement analysis. Indeed, if blast heat is prolonged beyond two or three minutes, loss may ensue. This is especially so, if the phosphate, after blasting, shows signs of fusion.

If the double precipitation of magnesium is to be retained, I do not deem it at all essential that the procedure given by the committee be followed. That procedure, of Wolcott Gibbs, is designed to give a precipitate of normal composition, but if a second precipitation is to follow, it is immaterial whether the first is of normal composition or not, so long as all is precipitated. Therefore, it does not seem logical to boil with the precipitant in an acid solution before rendering ammoniacal, when the object can be more simply attained. The amount of precipitant should be largely reduced if a single precipitation only is intended, and it is unnecessarily large, in any case.

Application of Corrections to the Foregoing Determinations.—With good work, little is gained in analyzing cements by correcting the ignited silica and alumina for the contaminations which they invariably contain, provided two evaporations and filtrations have been made for silica. It is also shown on page 1191, however, that the one correction should not be made without the other, for then the errors on the alumina may be large, especially where, as is most always the case, glass vessels are used for the precipitations.

The bisulphate correction for silica in the alumina must be made, not in the usual way, but, in order to avoid serious error, as follows: The bisulphate fusion is to be dissolved in water to which a good deal of sulphuric acid is added, and then evaporated

in platinum and heated till acid fumes are copiously given off. When cool, the pasty mass is redissolved in water, digested till all but the flocculent silica is in solution, then filtered. The ignited and weighed silica is to be checked by hydrofluoric and sulphuric acids, like the main silica.

I have recently followed J. Lawrence Smith's strong recommendation to use the sodium acid-sulphate for this purpose instead of the potassium salt, and with very good results. There is then no difficultly soluble potassium-aluminum sulphate to dissolve before filtering off the silica, but solution is speedy, and, furthermore, the action of the sodium salt on the ignited iron-aluminum oxides is more energetic, so that much time is saved by its use. There is, however, the disadvantage that the salt is far more difficult to keep in fusion than the potassium salt, so that the progress of solution of the oxides on the bottom of the crucible cannot be so well followed.

Sulphur.—Notwithstanding some adverse testimony from another source than the chemists who have participated in these series of analyses, I am fully of the opinion that the practice of not first removing silica where small quantities of sulphur are in question is perfectly safe. The only condition is that the silica must not be allowed to gelatinize, and this I never have the slightest difficulty in maintaining, first by using not very strong acid for effecting solution and then by diluting freely as soon as solution is accomplished. The vessel may then be placed on the steam-bath or even boiled on the iron plate without fear of gelatinization resulting. This mode of procedure avoids the contamination by sulphuric acid from the flame of a water-bath that is heated by gas, which is certain to result if the silica is first dehydrated in the usual way. When an oxidizing fusion of the cement or mixture is made, the asbestos or platinum-asbestos protection, mentioned in the paragraph below, should be used.

Ignition Loss.—Instead of igniting over a free blast-flame, the covered platinum crucible should be inserted about two-thirds of its depth into a close-fitting hole in asbestos board, or, better, in a disk of platinum foil which itself covers a large hole in asbestos board. The flame should strike at an angle of about 45° , and, when using the disk, for thirty minutes with 1 gram of slurry or limestone mixture, and five to ten minutes with a cement. Even

with only a good Bunsen lamp (using the disk) practically the same result can be reached in sixty minutes on a slurry or limestone and in thirty minutes on a cement. With a hot, closed muffle, ten minutes' time suffices with either raw mixture or cement, the crucible being placed about two inches from the door.

But each chemist should ascertain for himself, by direct experiment, what his blast or muffle can do, and this he can best learn by experimenting with a standard material whose composition is known. It would be, in my opinion, of great advantage to all cement chemists if the committee would see to the preparation of a large sample of limestone mixture, sufficiently large to last for many years, which could be issued to all applying for it. I select limestone instead of slurry or cement on account of its unchangeability under varying atmospheric conditions.

CONCLUDING RECOMMENDATIONS.

Probably the most fruitful plan for arriving at a method of procedure that would best suit the conditions prevailing in the majority of cement works would be through a subcommittee or a new committee of not more than three well-selected members, who should not only be analytical chemists, but men familiar with cement works. Now that the conditions governing accurate work are understood, such a committee should be able, by actual experiment on a standard sample like that mentioned above, to work out a detailed scheme of analysis that would be a satisfactory compromise between the imperative demands of the factory for immediate results, on the one hand, and a proper regard for reasonable accuracy on the other. Such a method might be known as the "factory control method," while for more precise work one of greater refinement might be given in detail and its employment strongly recommended, if not prescribed. While I agree, in general, with Messrs. Stanger and Blount in thinking that the consulting chemist, at least, should be untrammelled in the choice of his methods, it is, nevertheless, unfortunately true that no general analytical chemist is or can be equally familiar with all lines of work, nor are all of equal judgment in the selection of methods. Men of skill and judgment can often arrive at like results by diverse routes, but it is certain that this is not yet so with respect to all of the stages of a silicate analysis, even so simple a one as that of cement, and till this condition is

reached I think it were well to prescribe the procedure at certain stages.

But, after all, no amount of careful attention to any analytical process is of much avail unless the materials used are of good quality. Too many chemists, as appears from the replies furnished in the present case, assume, without positive knowledge, that those used by them are satisfactory; others report one or the other as of good quality without giving any quantitative data in support of such an assertion. No chemist can be said to do justice to his employers or patrons who does not *know* what order of error his results may include, arising from impurities in reagents and the solvent action of those reagents on his utensils, or from other causes either preventable or admitting of exact correction. Too often, beyond doubt, is a known contamination thoughtlessly excluded as negligible when, in fact, a quantitative test might have shown the falsity of the belief.

FOURTH SESSION OF THE INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS.

HELD IN BERLIN, GERMANY, JUNE 4, 1903.

Received September 22, 1903.

The following were present:

Professor Dr. A. Herzfeld, chairman.

Privy councilor, Prof. Dr. Landolt, Berlin.

Baron von Donner, chairman of the *Verein der am Zuckerhandel beteiligten Firmen*, Hamburg.

Privy Councilor Koenig, chairman of the board of directors of the *Verein der Deutschen Zuckerindustrie*, Berlin.

Professor Dr. Brodhun, representative of the *Physikalisch-Technische Reichsanstalt*, Berlin.

Professor Dr. Schoenrock, *idem*, Berlin.

Privy Councilor Professor Dr. von Buchka, delegate of the *Kaiserliche Reichsschatzamt*, Berlin.

Government Councilor Weinstein, representative of the *Kaiserliche Normal Aichungsamt*, Berlin.

Government Councilor F. Strohmer, Vienna, Austria.

J. Ragot, director of the *Syndicat des Fabricants de Sucre de France*.

K. Fischmann, director of the Russian Sugar Manufacturers' Association, Kiev.

Dr. Raschkowitsch, director of the chemical laboratory of the Russian Sugar Manufacturers' Association, Kiev.

François Sachs, representative of the *Société Technique et Chimique de Sucrerie de Belgique*, Brussels.

Dr. F. G. Wiechmann, representative of the American Sugar Refining Company, New York.

E. Silz, representative of the *Association des Chimistes de Sucrerie et de Distillerie de France*, Paris.

A Watt, member of the Beetroot Sugar Association of Lancashire, Liverpool, England.

S. Stein, member of the Beetroot Sugar Association of Lancashire, Liverpool, England.

Also the following members of the Commission :

Dr. C. Ahrens, Hamburg ; Lobry de Bruyn, Amsterdam ; Professor Dr. Frühling, Braunschweig ; Dr. G. Götting, Breslau ; Dr. B. Hermann, Hamburg ; F. Herles, Prague ; Dr. A. Langfurth, Altona ; Dr. O. Wendel, Magdeburg ; Dr. R. Woy, Breslau, as well as numerous other chemists connected with the sugar industry.

After the opening of the session, the chairman expressed his special thanks to Privy Councilor Landolt, the scientific founder of the polariscopic method, as well as to Baron von Donner, and to Privy Councilor Koenig, for their coming. The chairman then outlined the previous work of the Commission.

He requested Mr François Sachs, of Brussels, and Dr. F. G. Wiechmann, of New York, to again undertake the editing of the French and of the English text of the proceedings.

The sets of quartz-plates which had been selected by the *Physikalisch-Technische Reichsanstalt* in Berlin, and which had been tested in the laboratory of the *Verein der Deutschen Zuckerindustrie* as to their sugar value, have been distributed to proper central stations of the countries interested, and there are kept at the disposal of chemists. These plates have been tested in almost all of the countries which have received the sets, and have been

found correct. Some of these stations have thus far not made a report as to the results of this reexamination, and such a report is, therefore, requested.

Execution of the Paris agreement, according to which chemically pure sugar is to be used for the adjustment of polariscopes and for the testing of plates, has, in some countries, met with difficulties because they could not succeed in preparing chemically pure sugar. The laboratory at Berlin, therefore, offers to furnish chemically pure sugar.

In the determination of invert-sugar, a difficulty has arisen, inasmuch as the English chemists have, of late, again declared against the clarification with basic lead acetate; the Commission will, therefore, have to seek means and methods to prevent, in this respect, loss of uniformity, now secured in the methods of analysis.

THE DAY'S PROCEEDINGS.

(I) "Report concerning practical experiences made with the uniform methods of analysis agreed upon in Paris."

Doctor Hermann delivered an address on this topic; this is published in the *Zeitschrift des Vereins der Deutschen Zuckerindustrie*. The speaker was of the opinion that numerical proofs of the success of the Paris agreement could not be adduced, yet the fact could be stated that the differences have decreased in number. To avoid a warming of the polariscope tubes in handling, he recommended covering the same with rubber.

Privy Councilor Professor Dr. von Buchka made the following statements:

The International Commission for Uniform Methods of Sugar Analysis decided, in the year 1900, that the determination of invert-sugar in raw sugars is to be carried out according to the method of Prof. Dr. A. Herzfeld. It seems desirable to abandon this method and to prepare Fehling's solution in such a manner that the weighed constituents be brought into solution with water, up to one liter. This would be in accordance with the method otherwise customary in the preparation of normal solutions. This method of procedure has, moreover, been adopted in the official directions for the analysis of wine, decreed in Germany in the year 1896. It seems desirable that the manner of preparing Fehling's solution be always the same, whatever purpose the sugar determinations may have to serve.

Professor Dr. Herzfeld replied that Herzfeld's method differs from the method used in the examination of wines, not only in the manner of preparing Fehling's solution, but also in the employment of a definite heating surface. A further essential difference is the fact that the reaction is suddenly interrupted after two minutes by the introduction of cold water. On this account all tables which have been prepared by Meissl and others are of no value, unless one is also willing to return not only to Soxhlet's Fehling's solution, but also to the antiquated working methods for which these tables have been established.

In the determination of invert-sugar, the 10 grams of cane-sugar which are dissolved in Fehling's solution exert a great influence on the amount of copper reduced. It would, therefore, be dangerous to alter the concentration of the solution before this influence shall have been carefully studied, and a decision arrived at as to whether it might not be necessary to establish a new table for the solutions made thus differently.

Mr. Pellet declares himself as opposed to the use of basic lead acetate as a clarifying reagent, and for the heating of the solution to reduce the copper on the water-bath, instead of over the naked flame.

Government Councilor Strohmer believed that he might declare in the name of the Austrian chemists that they agree with the remarks made by Professor Herzfeld, for a change in the manner of preparing Fehling's solution would necessitate a change of tables for the determination of invert-sugar, that is to say, would amount to a change of the method itself. Commerce has adopted Herzfeld's method. Each produce-exchange demands, in the certificate, determinations of invert-sugar according to Herzfeld. If the method were to be changed, the consent of commerce would have to be secured. It was the determination of invert-sugar which held back, for so long, the introduction of uniform methods, and Mr. Strohmer expresses the wish that this agreement, which was so difficult to bring about, may not again be disturbed so soon by the introduction of a new method of preparing Fehling's solution. Dr. Woy next presented an additional report (*ad. 1.*) of the day's program. He, too, is unable to present data which cover all Germany, but in a compilation of Silesian analyses, made in duplicate, he made the observation that series of analyses which

were in excellent agreement were suddenly interrupted by series which exhibited serious differences, and that in such cases the super-analysis also did not tally with the series of the former analyses, but at times represented an accurate average. In such cases only the samples can have been the cause of the differences.

He recommends the collecting of such cases in order to determine, numerically, how often greater differences arise and whether, in such cases, the fault is to be ascribed to the method, the analyst, or the taking of the sample. Furthermore, he desires a more exact definition of the maximum amount of basic lead acetate, and of aluminum hydrate, allowable, in order to exclude, as far as possible, the source of error inherent in the volume of the precipitate.

Dr. Koehler-Maltsch was of the opinion that differences which still occur in polarizations must be ascribed to faulty graduation of the flasks.

The Commission decided to elect a Sub-commission for the elucidation of the questions at issue. This Sub-commission is to consist of Messrs. Watt, Wiechmann and Strohmer, and is to study especially the question of clarification by basic lead acetate, as well as the question of a change in Fehling's solution. Privy Councilor von Buchka promises his assistance in these investigations.

(II) "The valuation of 'Sand' and 'Krystallzucker' in International trade."

Government Councilor Strohmer, of Vienna, discussed this question. His lecture is printed in the *Zeitschrift des Vereins der Deutschen Zuckerindustrie*. The address evoked no discussion.

(III) "Introduction of International uniform directions for sampling raw sugars." Mr. Wiechmann stated that he considered it to be very desirable that a 100 per cent. sample be taken, that is to say, a sample from every package wherever this may prove at all possible. Furthermore, he added that great attention ought to be paid to the manner in which samples are taken, for, otherwise, very peculiar results would be secured, especially with raw sugars of lower grades.

Director S. Stein, Liverpool, explained that in England sugar, on importation, has to pay duty according to polarization. It is of

great importance that for this purpose the same sample be used which is used in effecting the purchase. The English authorities found very marked differences between their analyses and the results which the refineries declared. The cause of this is to be sought in the different manner of sampling the sugar. It is very difficult to obtain a correct average sample, especially of cane-sugar. As is known, cane-sugar is put up in different kinds of packages. For instance, in bags, in mats, in hogsheads, etc. Furthermore, a cane-sugar is not homogeneous, but varies in composition in different parts of the package. Thus, in cane-sugar, syrups and semifluid masses occur. All this has to be taken into consideration. It is necessary that the sampling be done in such a manner that the sample drawn be truly representative of the sugar. Sampling shall be done in such a way that the sample shall be taken from different parts of the package, and at one time. It is well known that stored sugar changes its composition. A sugar which has a certain composition to-day has a different composition one or two months hence. It is also necessary that the sampling be done on a given number of bags or packages. Mr. Stein, therefore, advised the adoption of a resolution or the addressing of a request to the International Commission to consider what points of view should necessarily be borne in mind in order that uniform sampling, especially of cane-sugars, may be achieved. The speaker is confident that the conclusions of such a forum, in this most important matter, would prove binding and elucidating.

At the request of the chairman, Mr. Wiechmann agreed to prepare a compilation of the different directions which are in force in the various countries interested in the sugar industry, and to submit this preliminary report to the Sub-commission, consisting of Messrs. Wiechmann, Watt and Strohmer.

It was the general opinion that it was necessary to consult expert chemists more than has been done heretofore in the drawing-up of working directions for samplers.

(IV) and (V) "Influence of temperature on the specific rotation of sucrose," and "Introduction of temperature-corrections when the temperature of observation differs from the temperature of 20° C., which has been accepted as the normal temperature." These two topics were disposed of together.

Dr. Schoenrock discussed the first-named of these subjects. His address is printed in the *Zeitschrift des Vereins der Deutschen Zuckerindustrie*.

In the discussion of this address, Mr. Wiechmann, while expressing appreciation of Schoenrock's labors, declared against the introduction of corrections to polarizations obtained in actual practice. Professor Herzfeld took the same position, because, besides the variations in specific rotation, still other factors come into play, for instance, the variable amount of evaporation which takes place on filtering the solution.

Professor Brodhun remarked that, if correct corrections are applied, correct results must be obtained. It was decided that the individual members of the Commission, for the present, are to study the question of corrections on their own account.

(VI) "Determinations of the sugar subject to duty or bounty contained in saccharine products and fruit preserves."

In this connection, the chairman read a paper prepared by Mr. H. W. Wiley, of Washington, who, to the regret of those assembled, was prevented from attending. The chairman closed his remarks with the words that the point of view taken by Mr. Wiley would probably meet with the unanimous approval of the Commission. There was no objection to this comment.

(VII) "Chemical control as an aid to the Entrepôt-system sanctioned by the Brussels convention."

The printed address of Professor Herzfeld, on this subject, was in evidence. It also appeared in the *Vereinszeitschrift*. There was no debate on this address.

The following papers, which figured on the program of the Congress of Applied Chemistry, were also disposed of during the session of the Commission.

(1) Lecture of Mr. Wiechmann on "A restant source of error in optical sugar analysis." The question of the influence of the basic lead acetate precipitate, discussed by Mr. Wiechmann, is to be further studied.

(2) Lecture of Mr. Dupont: "Sur l' unification des échelles saccharimétriques et l'adoption d'une échelle á poids normale de 20 grammes."

Mr. Dupont was not present. Decision on his proposition to introduce a normal weight of 20 grams is deferred.

(3) and (4) A paper by Mr. David R. Davoll: "A study in the determination of raffinose," and a paper by the same, "Should raffinose be considered as non-sugar in calculating the quotient of purity?" were presented in print. There was no discussion of these papers.

(5) A lecture by Mr. Sachs: "Shall chemical measuring instruments be graduated according to the old Mohr method, or according to the new official method of France and Germany?" A discussion followed this address. Professor Weinstein and Privy Councilor von Buchka stated their opinion to be that a single section should not adopt a resolution in this matter, and declared a return to Mohr's method a step backwards. Mr. François Sachs disputed the latter assertion.

The meeting then adjourned.

F. G. WIECHMANN, *Secretary*.

NOTE.

On the Emulsifying Action of Soap.—Experiments on the emulsifying power of soap solutions have been recently published by H. W. Hillyer.¹ In these it is shown that the effect is due to the lowering of the interfacial tension at the interface oil-soap solution, caused by the non-hydrolyzed soap contained in the aqueous solution. The variation of interfacial tension with the concentration of the soap solution was quantitatively studied by Hillyer by means of a dropping pipette.

It may be remarked, however, that not only have exactly similar conclusions been arrived at previously by me, but they have been obtained by an almost identical method and published in one of the most universally read scientific journals.²

Doubtless my paper must have escaped Mr. Hillyer's notice, for in his second paper he refers to himself as a pioneer. In my experiments, drops of a neutral, fatty oil (or of a neutral hydrocarbon oil) containing a specified amount of free aliphatic acid were allowed to ascend through an alkali solution of known strength. My first experiments (not published) were made by

¹ This Journal, 28, 511, 524 (1903).

² *Ztschr. phys. Chem.*, 31, 42 (1899).

allowing drops of a neutral oil to ascend through an aqueous soap solution, but this method was abandoned in favor of the former one, owing to uncertainty as regards the amount of hydrolysis in the soap solution. If Mr. Hillyer will refer to a recent paper by Krafft,¹ which also seems to have escaped his notice, he will find that a perfectly pure "soap" solution will *not* emulsify a neutral oil. This effect appears to occur only when the soap solution contains an excess of free alkali (or even alkaline chloride). From this it would seem that the lowering of interfacial tension and consequent emulsification are due to the production at the interface of a colloidal layer or membrane.

In conclusion, although Mr. Hillyer's paper forms an interesting contribution to an interesting subject, it is necessary to point out that neither his main conclusion nor the method by which it was obtained, is new.

F. G. DONNAN.

ROYAL COLLEGE OF SCIENCE, IRELAND,
August, 1903.

NEW BOOKS.

CHEMISTRY OF THE DYE-STUFFS. BY DR. GEORG VON GEORGIEVICS, Professor of Chemical Technology at the Imperial and Royal State Technical School at Bielitz. Translated from the second German edition by CHARLES SALTER. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1903. vi + 402 pp. Price, \$4.50 net.

This book, originally designed to form a section of a text-book on the "Technology of the Textile Fibers," was afterwards modified into a separate volume, chiefly in order to render it more accessible to chemists interested in the chemistry of dye-stuffs rather than in the dyeing and cloth-printing industries. For this reason, all particulars relating to the application of the dye-stuffs are relegated to the author's companion volume—"Chemical Technology of the Textile Fibres."

The aim of the author has been to provide a text-book presenting to the student, in as lucid and condensed a form as possible, the extremely wide domain of the modern chemistry of the dye-stuffs.

¹ *Ztschr. phys. Chem.*, 38, 371 (1902).

Care has been taken to bring into prominence all the relations known to exist between the various dyes and groups of dyes, as well as the connection between color and constitution, as the proper appreciation of these relations form the main object of the study of the chemistry of the dye-stuffs. An endeavor has also been made to clearly define the true importance attaching to the several dye-stuffs, whether theoretical, practical, or historical.

Owing to the rapid progress made in connection with the dye-stuffs since the appearance of the first edition of this book, the sections dealing with the azo dyes, the triphenylmethane dyes, the phthaleins, and the azines have been considerably modified, while those treating of the flavones and the sulphur dyes are entirely new.

The author has had the advantage of the very valuable assistance of Dr. C. Duisberg, Director of the Farbenfabriken, formerly Friedrich Bayer & Co., of Elberfeld, in reading the manuscript of both editions.

The book is an excellent one and can be heartily recommended to those desiring to study the chemistry of the dye-stuffs. The translator has, however, omitted several features of the original and thus made the translation decidedly inferior to it. For example, in the original only the most important facts are printed in large type, detailed information being given in smaller type. This was of great advantage to the beginner, as he could omit that part of the book printed in small type and yet have a complete survey of the subject. In the translation, everything is printed in the same type, whether it is important or unimportant, and in several instances information, which in the original was contained in foot-notes, has been put into the body of the book.

Again, the table of abbreviations, contained in the original, has been left out of the translation, but the abbreviations are used. This is a very important matter, for these abbreviations are used on nearly every page of the book. How is a student to know, without being told, that the letters B. or B. A. S. F. after the name of a dye-stuff mean that that dye is made by the Badische Anilin und Soda Fabrik.

The special literature of the dye-stuffs, given at the end of the book, has also been omitted from the translation, so that, if the reader is interested in a particular group of dyes and wishes to know where the original sources of the information contained in

the book are to be found, he would have to go to the German edition of the book.

The translation contains several inexcusable mistakes. For example, on page 3 the statement is made that aniline is a dye-stuff, and on pages 52 and 53 that nitroso-compounds are formed when *sulphurous acid* is allowed to act on phenols. The German terms benzol and toluol are used throughout the book in place of benzene and toluene. On pages 62 and 63, sodium *nitrate* is used for sodium *nitrite* in diazotizing salts of primary amines.

Those who read German at all readily, will find it advantageous to purchase the German edition of the book. For those who read only English, the translation is the best book on the subject now available, notwithstanding the many errors of translation.

W. R. ORNDORFF.

LES DÉRIVÉS TARTRIQUES DU VIN. PAR LE DR. P. CARLES. Troisième Edition. Bordeaux : Feret et Fils ; Paris : Libraires Associés, Editeurs. 1903. 169 pp. Price, 4 fr. 50. Franco poste, 4 fr. 80.

The brochure before us, in its third edition, offers the results of years of study and practice in the recovery and utilization of the tartaric products obtained from wine and its residue, and its value has been recognized by the Institut de France in the award of the Montoyon prize of 2000 francs to the author. It is well worthy of the careful consideration of those interested in tartaric materials. In his valuable little work, Dr. Carles discusses the methods whereby these products are recovered and the different forms in which they are sent to the market. This is followed by thorough discussion of the analytical methods—described in detail—which are employed for the valuation of the various crude products. Generally these consist in (1) determination of the quantity of potassium bitartrate (the “actual test” of the United States), (2) the determination of the total tartaric acid present as potash and lime salts (“total test”).

The first is comparatively simple and, according to Dr. Carles, as well as in the experience of the reviewer, gives accurate results. The second is complicated by the presence of various foreign substances in the crude tartars, and the method of Goldenberg, Geromont & Co., most widely employed, often gives results which,

according to Dr. Carles, are low in proportion to the quantity and character of the non-tartaric constituents in the material to be tested. To avoid these difficulties, Dr. Carles has devised a method in which the total tartaric acid is precipitated and weighed as tartrate of lime.

Discussing the choice of methods to be employed, Dr. Carles says: "Reviewing what has been said, we see that we must separate and determine.

"1. Potassium bitartrate alone.

"2. Tartaric acid existing in mixtures of potassium bitartrate and calcium tartrate.

"3. Tartaric acid existing as tartrate of lime.

"For potassium bitartrate alone, in form of crude tartar, the same value is to be accorded to the methods of Teschemacher, Klein, and the 'Actual.'

"For lees, particularly low-grade, viscous and gummy, the American 'actual test' is the best.

"For mixed tartrates, with predominance of bitartrate, of value simply for the content of tartaric acid, the Goldenberg method of 1898 is to be recommended.

"When tartrate of lime is of importance or predominates in a crude tartar, the method of Carles, of 1903, is preferable.

"For factory residues, containing phosphates of iron, lime and alumina, plaster and tartaric acid, in unknown forms, there is little choice between the method of Goldenberg of 1898 and that of Carles of 1903."

The author, furthermore, discusses adulteration of crude tartars, a subject of interest and importance to refiners. In addition to this, attention is given to the many details of the tartar industry, offering information obtained by long experience and of value to all interested in the important industry under consideration.

In his letter, transmitting his book, Dr. Carles says: "I shall be happy to send other copies of the book to those of your members who may wish it, or to those of your manufacturers, who may ask for it." It is practically the sole authoritative exposition of the subject, and it is, therefore, of great practical value.

WM. McMURTRIE.

DESCRIPTIVE CHEMISTRY. BY LYMAN C. NEWELL, PH.D., Instructor in Chemistry, State Normal School, Lowell, Mass. D. C. Heath & Co. 1903. 590 pp.

The success of the author's "Experimental Chemistry" caused the issuance of a readable "Descriptive Chemistry" from the same publishers. The book is divided into two parts: The first "contains the text, together with exercises and problems"; the second gives the experiments (179 in number). To the former is added an appendix with the metric system, valuable problems, enough of crystallography, some history and biography, table of atomic weights, and a wholesome list of reference books. To the second is added sane advice concerning equipment of the laboratory and generous, but economic, utilization of the necessary chemicals for the course given.

In passing opinion upon a book of this class, one is confronted with the extreme points of view advocated for an elementary course in chemistry; *viz.*, it should be for the accumulation of a large number of facts or for general culture purposes and training in scientific methods. It is a distinct success in the former and does not fail in the latter, altogether. Decidedly, the modern trend has been to follow the periodic system (whether it be true or not, is not the question), or quickly lead to it. In this book, the periodic classification of the elements is arrived at only after one has read 398 pages, just 38 pages before the close of the text proper.

The use of formulas is so gradually introduced that the student does not become frightened. Chapter IX, on Equivalents, Quantitative Significance of Equations, is particularly clear, while Chapter X, on Light, Heat, Electricity and Chemical Action, is clever and holds the attention.

Regarding the theory of electrolytic dissociation or ionization, one would prefer reading "most recently put forward" instead of "now generally held." Many of the modern practices are clearly explained in large type, often with illustrations, as, for example, the Castner process. Fine print suffices for the Leblanc and Solvay processes.

The arrangement which brings into consideration the carbon oxides, cyanogen, sulphocyanates and potassium ferrocyanide before methane, etc., or even before the student has been introduced

to sulphur, may be questionable, or only a matter of opinion. On page 18, the negative sign is omitted before the figures for the boiling-point of oxygen. All sapphires are by no means blue.

We like the remark under the photogravure of Joseph Priestley, "the discoverer of oxygen," better than that under Sir Humphry Davy, "the famous English chemist whose brilliant discoveries have never been surpassed."

The experiments in Part II are not only carefully selected, but are accompanied with searching questions. To be sure, in some cases (p. 485), the answers are given in the next paragraph.

The typography is all right and the index shows the care exercised in the making, for it is excellent. After all, *the* question to which a text-book should answer is, "Is it teachable"? The answer here is an emphatic affirmative. CHAS. BASKERVILLE.

SIMPLE METHOD FOR TESTING PAINTERS' MATERIALS. BY A. C. WRIGHT, M.A., B.Sc. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 163 pp. 8 illustrations. First Edition, 1903. Price, \$2.50 net.

The author states, in his preface, that the book is designed to enable the painter and paint-dealer to test and value the materials they buy, and the manufacturer and dealer the samples submitted to them, in the simplest manner, both in regard to practical properties and composition, the latter term used more in a manufacturing than in a purely chemical sense.

In a short introduction the author emphasizes the necessity of testing pigments and paints, and establishing and preserving reference standards. Some 30 pages are next devoted to a description of the apparatus and reagents to be used in the tests. The remaining 117 pages are devoted to a discussion of the mechanical and chemical properties and tests for impurities of dry and paste colors, liquid and gloss paints, varnishes, driers, linseed oil and turpentine.

A book of this kind must necessarily be incomplete and, to some extent, unsatisfactory. It is true that there are many tests for impurities and inferior or debased quality that can be made by the class to which this book is mainly addressed—dealers and practical paint-users—and confidence placed in the results. But, on the other hand, there are many varieties of paints and oils on the market whose quality can only be judged by the analyses of a

competent chemist, analyses that are too difficult and require too much apparatus to be attempted by the layman. The author recognizes this difficulty and very properly cautions against a charge of fraud on the part of the manufacturer or dealer, unless based on the analysis of a chemist.

The various tests given are, for the most part, qualitative, and in full detail, the varieties of paints most in use being treated at length. Besides the tests that are well known, several not in common use, are described. The book is well worth the price to the user of paints and contains much information on the subject that he will appreciate, and the general analyst also will find many points that will be of assistance in his analytical work. The proof-reading has been carefully done, though a few sentences read strangely—as where he speaks of the “efflorescence of carbonic acid” on warming lead carbonate with dilute nitric acid.

The printing and paper are up to the standard of the publishers, and the book has a good index.

FRANK JULIAN.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 77.]

DERIVATIVES OF COMPLEX INORGANIC ACIDS.

[THIRD PAPER.]

BY ALLEN ROGERS AND EDGAR F. SMITH.

Received September 25, 1903.

By REFERENCE to the American Chemical Journal, 7, 413, there will be found a classification of the various groups of "complex inorganic acid" derivatives obtained by Wolcott Gibbs—the pioneer in this field of research. There will not be observed in that grouping any derivatives in which there are four different acid radicals acting as a compound anion. It has been the purpose of the present investigation to ascertain whether dioxides could be introduced into complexes consisting of sesquioxides, pentoxides and trioxides. It was hoped that by boiling ammonium vanadophospho-tungstate with an excess of silicic hydrate such a result would be reached, but combination did not ensue. The various constituents were then separately brought together and boiled with an excess of ammonium hydroxide for a period of six hours. Some dioxide did enter the combination, but it was concluded to operate in neutral solution; accordingly, 30 grams of ammonium paratungstate, in 700 cc. of water, were boiled ten hours in the presence of an excess of the hydrate of the particular dioxide which it was desired to introduce, after which 2 grams of ammonium phosphate were added, the solution being then boiled

two hours longer, when 8 grams of ammonium metavanadate, reduced to the hydrate of the trioxide,¹ were added and the whole boiled for two hours more. This was the general method of preparation; hence, it will not be repeated in connection with the several derivatives which are described later.

In studying the behavior of these products, no tests were discovered which would differentiate one body from another. The following observations apply equally well to all. The salt separated from a concentrated aqueous solution in large, brilliant, black, octahedral crystals. These were very soluble in water, but were insoluble in organic reagents. Nitric acid, added to the solid salts, served to decompose them, a yellow-colored body resembling tungsten trioxide separating, but disappearing completely on the addition of water, and yielding a yellow-colored solution.

Dilute or concentrated nitric acid, added to the solution of the salts, merely caused a change in its color, without producing a precipitate. Hydrochloric acid caused a color change in the solution very slowly only on boiling.

Ammonium hydroxide did not alter the salt solutions. Sodium hydroxide produced a gray precipitate, which dissolved, on boiling, with the evolution of ammonia. A dark brown precipitate was produced by silver nitrate. It dissolved, to some extent, in boiling water. Ammoniacal silver nitrate produced an olive-green colored precipitate. It dissolved completely when the solution was boiled.

The precipitate, light green in color, formed by mercurous nitrate, was insoluble in water, but readily dissolved upon the addition of a few drops of nitric acid. The lead precipitate acted similarly. Mercuric chloride caused no precipitation. The same was true of copper sulphate, while a solution of ammoniacal copper sulphate produced a dirty gray precipitate, insoluble in boiling water. Cadmium chloride gave no reaction. Ammoniacal cadmium chloride threw out a dirty gray precipitate, insoluble in boiling water, but dissolved by water containing a few drops of hydrochloric acid. Cobalt nitrate, in ammoniacal solution, produced a bottle-green colored precipitate, which changed to an

¹ The hydrate of the trioxide is produced when ammonium meta-vanadate is boiled for half an hour with hydrochloric acid, then evaporating to dryness upon a water-bath. The residue, taken up in water, imparts to the latter a copper-green color. Ammonium hydroxide was added to the solution. The resulting precipitate (hydrate of vanadium trioxide), after being washed once or twice with dilute ammonium hydroxide, was introduced into the tungstate solution.

olive-green on boiling. Barium chloride, in neutral solution, was without any action, but in the presence of ammonia and upon boiling, threw down a heavy insoluble precipitate. In the analysis of the salts mentioned below, the method described in previous communications proved inadequate. The difficulties met in this portion of the investigation were great. They were, in the main, surmounted. After much search, with frequent failures, the following course was adopted and gave, it is believed, reliable results.

In each case the air-dried salt was gently and gradually heated to dull redness. The loss represented water and ammonium oxide. The residue was then fused with equal parts of sodium carbonate and potassium nitrate. The fusion was taken up with water containing ammonium hydroxide and ammonium nitrate, boiled for several minutes and then filtered. The insoluble portion was thoroughly washed, dried, ignited and weighed as MeO_2 . A "magnesia mixture" was added to the cold filtrate and washings. The magnesium ammonium phosphate was dissolved and reprecipitated. The tungstic acid, in the filtrate from the phosphoric acid precipitate, was determined according to the method of Gibbs, modified by Friedheim.¹ The vanadium was obtained by difference. The ammonium oxide was estimated in the usual manner.

A few words regarding the nomenclature, used in this communication, may not be out of place. An inspection of the literature relating to "complex inorganic acids" will disclose confusion on this point. After reflection, it was concluded to terminate the names of the dioxides, MeO_2 , in *oso*; those of the type of Me_2O_3 , in *ico*, and those of the form of Me_3O_5 , in *o* or *io*. It is admitted that this system is not satisfactory and is contradictory to our generally accepted ideas on the subject, yet it seems to be the only means of indicating a differentiation in the types of oxides in these complexes.

AMMONIUM SILICOSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.
$(\text{NH}_4)_2\text{O}$	5.42	5.37	5.40
SiO_2	0.56	0.67	0.68
V_2O_5	15.83	15.77	15.80
P_2O_5	1.33	1.35	1.34
WO_3	60.32	60.58	60.45
H_2O	16.41	16.26	16.32

¹ *Ber. d. chem. Ges.* (1890), p. 353.

AMMONIUM TITANOSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.	Per cent.
$(\text{NH}_4)_2\text{O}$	5.48	5.55	5.48	5.45
TiO_2	0.66	0.65	0.72	0.50
V_2O_5	18.98	19.10	18.89	18.87
P_2O_5	2.45	2.44	2.75	2.52
WO_3	56.29	56.08	56.50	56.42
H_2O	16.14	16.18	16.01	16.24

AMMONIUM ZIRCONOSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.
$(\text{NH}_4)_2\text{O}$	5.35	5.43	5.39
ZrO_2	0.63	0.59	0.61
V_2O_5	14.28	14.22	14.25
P_2O_5	2.49	2.55	2.52
WO_3	62.29	62.18	62.24
H_2O	14.96	15.03	14.99

AMMONIUM THOROSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.
$(\text{NH}_4)_2\text{O}$	5.42	5.40	5.41
ThO_2	0.77	0.80	0.79
V_2O_5	16.03	16.31	16.17
P_2O_5	2.52	2.71	2.61
WO_3	59.31	58.94	59.13
H_2O	15.95	15.84	15.89

AMMONIUM STANNOSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.	Per cent.
$(\text{NH}_4)_2\text{O}$	5.34	5.40	5.38	5.37
SnO_2	0.25	0.23	...	0.24
V_2O_5	12.33	12.47	...	12.40
P_2O_5	2.34	2.38	2.36	2.36
WO_3	65.51	65.29	65.20	65.40
H_2O	14.23	14.23	14.23

The reactions of ammonium vanadico-phospho-tungstate are vastly different from those obtained after the introduction of a dioxide into its composition, even if the quantity of that dioxide be small. In mineral analysis the influence of such minute amounts of supposedly adventitious constituents is too often disregarded and not considered in the deduction of formulas.

The reader will grant that there is in the above analytical results satisfactory concordance. The dioxide was extremely difficult to eliminate entirely from the remaining components of the anion, so that while it is thought the percentages given are correct, yet, if there be an error in this factor, when corrected, it will prove to be above rather than below the amount here given.

The formulas deduced from the preceding figures of analysis are imposing and appear rather improbable, so that, for the present, they can be omitted, as the introduction of other dioxides is projected. Efforts, too, are being made to find other means of arriving at the molecular magnitudes of these bodies.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 78.]

DERIVATIVES OF COMPLEX INORGANIC ACIDS.

[FOURTH PAPER.]

BY ALLEN ROGERS AND EDGAR F. SMITH.

Received September 25, 1903.

It may be observed that in those bodies containing vanadium but two oxides of the latter element appear—the trioxide and pentoxide. No derivatives of vanadicotungstic acid ($\text{H}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot \text{WO}_3$) have yet been prepared. In the classification of Wolcott Gibbs they are lacking. Further, the question had arisen whether by reduction of vanadic acid with hydrochloric acid the resulting oxide was really not the same as that produced on reducing vanadic acid with sulphur dioxide. If the stages of reduction were identical, then the hydroxides corresponding to these oxides— V_2O_3 and V_2O_4 —if combined with tungstic acid, would yield one and the same complex acid. As will be seen, the products were dissimilar.

AMMONIUM VANADICO-TUNGSTATE,



Thirty grams of ammonium paratungstate were boiled for six hours, when 6 grams of vanadium trioxide were introduced and the boiling continued for two hours longer. The filtered solution was reduced to a small volume and allowed to crystallize. Frequently, ammonium tungstate separated first and mixed with the vanadico-tungstate derivative. The crystals were treated several times with ice-water, which did not dissolve the ammonium tungstate, and, on evaporating the solution, ammonium vanadico-tungstate crystallized out in thin crusts, very soluble in water, but insoluble in organic solvents. The addition of nitric acid

to the salt solution changed the color from black to yellow, and tungsten trioxide separated. Hydrochloric acid caused a slight deposition of trioxide. Mercurous nitrate produced an olive-green colored precipitate, insoluble in boiling water, but dissolving upon the addition of a few drops of nitric acid. The silver salt was olive-green in color and only partially soluble in boiling water. Mercuric chloride and copper sulphate produced no precipitates in the neutral aqueous solution of the salt. Ammoniacal cadmium chloride and ammoniacal cobalt nitrate produced precipitates which were insoluble in water. They dissolved on the addition of a few drops of nitric or hydrochloric acid, with the deposition of tungsten trioxide. The barium salt was insoluble in boiling water.

In analyzing the salt, the Gibbs method, modified by Friedheim,¹ was adopted.

	Theory.	Found.		
		I. Per cent.	II. Per cent.	III. Per cent.
$(\text{NH}_4)_2\text{O}$	6.66	6.56	6.56	6.52
V_2O_5	6.40	6.44	6.39	5.91
WO_3	79.24	79.24	79.26	79.76
H_2O	7.70	7.79	7.79	7.81

AMMONIUM VANADOSO-TUNGSTATE,



Ammonium vanadate, in the presence of sulphuric acid, was reduced with sulphur dioxide and the solution precipitated with ammonium hydroxide. The resulting body, after washing, was added to a boiling solution of ammonium paratungstate. After filtering and evaporating to a small volume, black, well-defined, octahedral crystals separated. These proved to be very soluble in water. Nitric acid changed the color of the black solution to yellow *without*, however, *the separation of tungsten trioxide*. Hydrochloric acid does not change the color of the solution in the cold and only very slowly on boiling. No deposition of trioxide occurred. The mercurous salt was insoluble in pure water, but dissolved on the addition of a little nitric acid. The lead salt behaved in the same way. Mercuric chloride, cadmium chloride and copper sulphate were without action. The last two salts, in ammoniacal solution, did precipitate insoluble compounds, that

¹ *Ber. d. chem. Ges.*, 23, 353 (1890).

acids dissolved. Ammoniacal cobalt nitrate behaved in the same way. The barium salt, emerald-green in color and insoluble in water, dissolved on the addition of a few drops of acid.

Analysis:

	Theory	Found.		
		I. Per cent.	II. Per cent.	III. Per cent.
$(\text{NH}_4)_2\text{O}$	6.38	6.47	6.29	6.33
V_2O_5	8.15	8.30	8.28	...
WO_3	79.72	79.27	79.56	80.43
H_2O	5.75	5.96	5.87	...

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 79.]

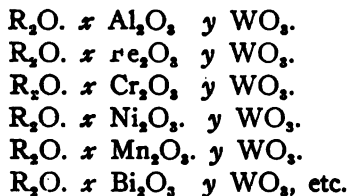
DERIVATIVES OF COMPLEX INORGANIC ACIDS.

[FIFTH PAPER.]

BY CLARENCE W. BALKE AND EDGAR F. SMITH.

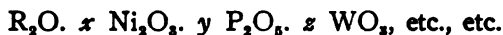
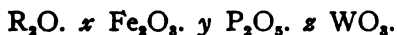
Received September 25, 1903.

FIFTY years ago Struve made double molybdates, which he believed were analogous to the alums. Wolcott Gibbs showed that the products of Struve's efforts were salts of "complex inorganic acids," in which the various sesquioxides, together with molybdenum trioxide, constituted the several anions in union with protoxides—cathions. It was Struve's intention to prepare analogous tungstates. He never described any of these and, in order to complete certain gaps in a line of inquiry, upon which we have been engaged, we undertook the preparation of compounds following the general types



All of these have been made. In this communication, however, we shall only describe those derivatives in which aluminum and bismuth oxide are present. The remaining bodies will be

further studied and efforts will be made to introduce certain other sesquioxides. We have also made a number of bodies of these types:



It may be mentioned that the introduction of the pentoxide apparently increased the stability of the resulting body and caused it to crystallize in a more definite and pronounced form.

AMMONIUM ALUMINICO-TUNGSTATE,



This salt was made by boiling freshly precipitated and thoroughly washed aluminum hydroxide, in excess, with ammonium paratungstate for from fifteen to twenty hours, when the solution was allowed to drain through a folded filter. On evaporating the clear liquid upon a water-bath, a dense, highly refracting sirup appeared. Glass floated on it. On exposure to the air, it dried to a semitransparent mass. It seemed to be a very stable body. Ammonium hydroxide added to its solution did not produce a precipitate. Its dilute solutions were not affected in the hot or cold by dilute hydrochloric or nitric acids.

The dry, powdered salt dissolved in concentrated nitric acid; precipitation did not occur, even upon boiling. The salt was soluble also in concentrated hydrochloric acid without the production, in the cold, of a precipitate, but when the solution was vigorously boiled a yellow-colored precipitate separated. Mercurous nitrate produced, in its aqueous solution, a yellowish white-colored precipitate. The precipitate caused by barium chloride was almost insoluble in hot water. After drying, acids failed to dissolve it. In a slightly ammoniacal solution of the salt, silver nitrate produced a yellowish white precipitate, which proved to be soluble in a large volume of hot water.

ANALYSIS.

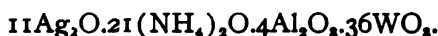
The powdered, air-dried salt was further dried by exposure, for several hours, to the temperature of a water-bath. A weighed portion was then ignited at a low red heat in a tared porcelain crucible. The loss it sustained represented water and ammonium oxide. The ignited material was next fused with potassium bisulphate. The fused mass was digested with 125 cc. of water,

15 cc. of nitric acid, and several drops of hydrochloric acid. When the decomposition was complete, the solution was filtered and the aluminum precipitated, with ammonium hydroxide, from the clear liquid. Whenever the resulting aluminum oxide was contaminated with tungstic oxide the fusion was repeated. The ammonium oxide was determined in the usual manner.

Results:

	Theory.		Found.		
	Per cent.	Per cent.	I. Per cent.	II. Per cent.	III. Per cent.
$3(\text{NH}_4)_2\text{O} \dots \dots$	156	6.45	6.61	6.45	6.42
$\text{Al}_2\text{O}_3 \dots \dots \dots$	102	4.22	4.12	4.17	...
$9\text{WO}_3 \dots \dots \dots$	2088	86.35	86.30	86.24	...
$4\text{H}_2\text{O} \dots \dots \dots$	72	2.98	2.97	3.14	...

SILVER AMMONIUM ALUMINICO-TUNGSTATE,



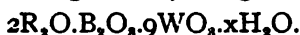
A yellowish white precipitate was produced when silver nitrate was added to a distinctly ammoniacal solution of the preceding salt. This precipitate was washed with cold water, in which it proved to be but sparingly soluble. Or, it was dissolved in a large volume of hot water, made ammoniacal. The filtrate was allowed to stand, when a crystalline mass separated from it on cooling. Analyses of the precipitated salt and the crystalline body showed them to be identical in composition. Air-dried samples were used for the analysis. The perfectly dry salt was quite insoluble in pure water, but readily soluble in water containing ammonia or nitric acid. Mercurous nitrate, introduced into the nitric acid solution, produced a yellowish white precipitate, readily soluble in hot water.

Analysis.—The silver was determined as chloride in the nitric acid solution of the salt, while the other constituents were estimated as described under the ammonium salt. The loss upon ignition was found to equal the ammonium oxide determined directly.

	Theory.		Precipitated salt.	Crystallized salt.
	Per cent.	Per cent.	I. Per cent.	II. Per cent.
$11\text{Ag}_2\text{O} \dots \dots \dots$	2552	20.57	20.71	20.48
$21(\text{NH}_4)_2\text{O} \dots \dots$	1092	8.80	8.87	8.90
$4\text{Al}_2\text{O}_3 \dots \dots \dots$	408	3.29	3.25	3.28
$36\text{WO}_3 \dots \dots \dots$	8352	67.32	67.17	67.34

If the sum of the protoxides be taken, the formula would read
 $32R_2O.4Al_2O_3.36WO_3$,
 which would furnish the simple formula
 $8R_2O.Al_2O_3.9WO_3$,
 when divided by four.

It may be observed here that Klein¹ has represented the most stable series of borico-tungstates by the general formula



AMMONIUM BISMUTHICO-TUNGSTATE,



On boiling well-washed bismuth metahydroxide with ammonium paratungstate for two days, it dissolved in large amount, so that it was necessary to make additions of it from time to time. The solution, filtered from the excess, had a yellow color. It was evaporated to complete dryness and the residue then exhausted with a small quantity of hot water, the solution filtered and allowed to cool, when ammonium bismuthico-tungstate separated as an oil, having a specific gravity slightly above 3.6. This oil, after being washed carefully several times with cold water, dried to a transparent, yellow-colored glass. No precipitate was produced on strongly diluting the solution of this salt with water. Ammonium hydroxide caused no change in its cold dilute solutions, but when the latter were boiled in the presence of ammonia, a copious white precipitate separated. Nitric acid caused no change in the boiling dilute solutions of the salt, but in concentrated solutions precipitation occurred on the addition of concentrated nitric acid. The addition of a large volume of hot water again effected solution. Hydrochloric acid occasioned no change in cold or hot dilute solutions, while tungstic acid separated on boiling with concentrated hydrochloric acid. Mercurous nitrate precipitated yellowish white mercurous bismuthico-tungstate. The results of the analysis were:

	Theory.		Found.		
	Per cent.	Per cent.	I. Per cent.	II. Per cent.	III. Per cent.
$3(NH_4)_2O$..	156	4.09	4.34	4.28	4.14
$2Bi_2O_3$	930	24.36	24.31	24.22	25.00
$11WO_3$	2552	66.83	66.59	67.07	66.31
$10H_2O$	180	4.72	4.76	4.43	4.50

¹ *Ann. chim. phys.* (5), 28, 350.

POTASSIUM BISMUTHICO-TUNGSTATE,



This salt separated in the form of a yellow-colored oil, upon adding a hot saturated solution of potassium bromide to a concentrated solution of ammonium bismuthico-tungstate. On cooling, the oil sometimes showed crystals which were very soft and gummy in appearance. It was discovered to be best, when the oil had become viscous and gum-like, to warm it again with a saturated solution of potassium bromide, after which it was repeatedly washed with small volumes of warm water. It was then dried on the water-bath to a transparent, pale lemon-yellow colored glass.

Analysis.—Except for the determination of the potassium the method pursued in the preceding analyses was adopted. In estimating the potassium, a weighed amount of the "glass" was covered with water and mercurous nitrate added in slight excess. Ammonium hydroxide was added to alkaline reaction, the excess of it being expelled by boiling. A few drops more of mercurous nitrate were introduced and, after standing half an hour, the precipitate was filtered off and thoroughly washed with warm water. The filtrate, after acidulation with dilute sulphuric acid, was charged with hydrogen sulphide. The filtrate from the mercury sulphide was evaporated and the potassium obtained as sulphate.

Results:

	Theory.		Found.	
	Per cent.	Per cent.	I. Per cent.	II. Per cent.
$3K_2O$	282	6.99	7.00	7.21
$2Bi_2O_3$	930	23.05	22.72	22.53
$11WO_3$	2552	63.27	63.84	63.88
$15H_2O$	270	6.69	6.44	6.38

STRONTIUM BISMUTHICO-TUNGSTATE,



This salt was made by transposing the potassium salt with a saturated solution of strontium chloride. The product was an insoluble yellow-colored oil, which was washed with hot water to remove all soluble impurities. When cooled, the oil changed to a yellow wax. It was insoluble in pure water, but dissolved readily upon the addition of a few drops of nitric acid. Dried

upon a water-bath, it changed to a hard, vitreous mass. The determination of the strontium was made as described under the potassium salt.

Results:

	Theory.		Found.	
	Per cent.	Per cent.	I. Per cent.	II. Per cent.
3SrO	311	7.79	6.80
2Bi ₂ O ₃	930	23.30	23.07	23.42
11WO ₃	2552	63.95
11H ₂ O	198	4.96	4.96	4.95

The purpose of this study will be to ascertain to what extent the more metallic sesquioxides can be introduced into such complexes as have been indicated in the preceding paragraphs, and to exhaustively investigate their derivatives before advancing to those compounds in which there will appear the additional pentoxide.

Columbo- and tantalio-tungstates of sodium and ammonium have been made and analyzed, but a description of them will be reserved for a later communication.

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THE INFLUENCE OF SOIL MOISTURE UPON THE CHEMICAL COMPOSITION OF CERTAIN PLANT PARTS.

By JOHN A. WIDTSOR.

Received October 7, 1903.

THE great variation in the chemical composition of plants grown under the same climatic conditions and upon similar soils, has always been a somewhat mystifying phenomenon to students of plant chemistry. That plant composition is influenced by soil composition is beyond question; and it is quite generally believed that sunshine, temperature and soil moisture are factors in controlling the chemical composition of plants. However, the relative and absolute values of these soil, climatic and water factors have not been determined, even approximately; and the observed variation in plant composition has usually been beyond satisfactory explanation. In view of this lack of knowledge, it was

most interesting to find a definite relation between the soil moisture and the chemical composition of plants.

In a series of exhaustive experiments on irrigation, carried on by the Utah Experiment Station, the water applied to plants was definitely controlled, and the quantity so varied as to determine the most economical use of water in an irrigated district. All the plants grown in the experiments were subjected to chemical analysis. The full report of the work, in the summer of 1901, is published in Bulletin No. 80 of the Utah Station, and it is upon some of the results there found that the present paper is based.

SOIL CONDITIONS OF THE EXPERIMENTS.

The farm upon which these experiments were conducted is located on the old fossil delta of the Logan River, in Cache Valley, State of Utah. The soil is very shallow—varying in depth from 9 to 59 inches, with an average depth of 28 inches. Below this thin layer of soil is a porous bed, nearly 300 feet deep, composed of coarse gravel, with occasional streaks of sand. It is most probable that this condition of shallow soil, with very porous subsoil, was a strong factor in producing the observed variation in the chemical composition of the crops grown upon the farm. The soil layer is, in most respects, similar to the soils that prevail within the Great Basin Region, as shown by the following physical and chemical analyses. The methods of analysis followed were those prescribed by the Association of Official Agricultural Chemists.

TABLE I.—PHYSICAL COMPOSITION OF THE SOIL.

Depth.	First foot.	Second foot.	Third foot.
Medium sand (0.1 to 0.5 mm.).....	28.1	29.7	31.6
Fine sand (0.032 to 0.1 mm.).....	25.6	26.4	29.6
Coarse silt (0.01 to 0.032 mm.).....	19.2	16.4	14.6
Medium silt (0.0032 to 0.01 mm.)..	10.2	6.6	6.6
Fine silt (0.001 to 0.0032 mm.).....	2.6	5.6	6.5
Clay (below 0.001 mm.).....	8.4	8.8	8.6
Moisture	4.7	4.3	1.8
Soluble and lost	1.2	2.2	0.7
Total.....	100.0	100.0	100.0
Average weight of one cubic foot of dry soil	88.9 lbs.		
Average absolute water capacity	28.56 per cent.		

TABLE II.—CHEMICAL COMPOSITION OF THE SOIL.
(All per cents. are referred to the water-free soil.)

	First foot.	Second foot.	Third foot.
Insoluble matter.....	68.42	65.66	56.49
Potash, K_2O	0.65	0.57	0.43
Soda, Na_2O	0.55	0.53	0.60
Lime, CaO	6.07	8.20	14.81
Magnesia, MgO	5.13	4.13	3.32
Alumina, Al_2O_3	3.13	2.36	2.39
Iron oxide, Fe_2O_3	2.33	2.65	1.72
Phosphoric acid, P_2O_5	0.20	0.15	0.24
Sulphuric acid, SO_3	0.10	0.11	0.08
Carbon dioxide, CO_2	10.00	12.74	17.90
Organic matter.....	3.86	2.99	2.12
Total.....	100.44	100.09	100.10
Humus.....	3.72	1.18	1.06
Nitrogen.....	0.149	0.100	0.072
Water at 100 C.....	1.85	1.91	1.69

The plats devoted to these experiments were one-twentieth of an acre in area, well ridged around the edges, so that the water applied would cover the ground to an approximately uniform depth. The depth of water applied at one irrigation varied, ordinarily, from 5 to 7.5 inches. All plants in the same experimental set were treated alike, except as to the quantity of water applied. The amount of water applied is expressed in the depth in inches to which the plats would have been covered had it been applied at one time.

MAIZE KERNELS.

The maize used was of unknown name, but had been grown for many years on the Station farm. It was sown on April 30th, and throughout its life exhibited no extraordinary characteristics, save the variation due to the application of varying amounts of water. The ripe maize was harvested on September 11th. The maize kernels were analyzed with the following results:

TABLE III.—PERCENTAGE COMPOSITION OF MAIZE KERNELS.

Irrigation water applied. Inches.	Water in fresh substance.	Water-free substance.				
		Ash.	Protein.	Ether extract.	Crude fiber.	N-free extract.
7.5	14.01	1.62	15.08	6.02	1.89	75.39
10.0	11.00	1.59	13.42	5.39	2.23	77.37
15.0	11.66	1.65	13.48	6.16	1.91	76.86
20.0	13.00	1.56	12.83	6.29	2.19	77.14
37.3	14.36	1.62	12.52	6.26	1.89	77.72

With one exception, the per cent. of water increased regularly with the increase in the amount of water under which the maize was grown. The per cent. of ash is not regularly affected by the quantity of water used. The protein content is strikingly influenced by the amount of water added to the soil. As the water increases, the per cent. of protein decreases—the difference between the protein content of maize which received 7.5 inches of water and that which received 37.3 inches being 2.56 per cent. The percentage of ether extract was also slightly affected by the soil moisture. As the water applied to the soil increases, the ether extract increases, also.

The per cent. of crude fiber does not seem to be regularly influenced by the soil moisture, but the N-free extract tends to increase on the well-watered plats. In general, the protein in the maize kernel decreases with increased applications of water, while the ether extract and N-free extract increase.

OAT KERNELS.

The variety of oats used in this experiment was "American Banner." The seed was placed in the ground on April 20th, and the ripe crop was harvested on July 30th. The composition of the oat kernel is shown in Table IV.

TABLE IV.—PERCENTAGE COMPOSITION OF OAT KERNELS.

Irrigation water applied. Inches.	Water in fresh substance.	Water-free substance.				
		Ash.	Protein.	Ether extract.	Crude fiber.	N-free extract.
6.98	8.00	3.26	20.79	3.91	9.02	63.02
13.20	7.73	4.52	17.29	4.19	10.76	63.25
14.89	8.11	4.97	15.48	4.21	15.40	59.55
30.00	8.40	4.49	15.49	4.59	10.92	64.51
40.00	8.62	4.55	15.80	4.56	10.38	64.71

As in the case of corn, the per cent. of water in the fresh substance is increased by an increased amount of water. The per cent. of ash does not seem to be affected by the soil moisture. As in the case of corn kernels, the relative amounts of protein are strongly affected by varying the amount of water applied to the soil. The larger the quantity of water, the smaller the per cent. of protein. The highest and lowest per cents. are 20.79 and 15.48—a difference of 5.31 per cent.

The per cent. of ether extract is highest in the well-watered plats, and the variation follows quite regularly the amounts of

water used. The difference between the highest and lowest per cent. is 0.68. The highest per cent. of crude fiber is found on the plat receiving an intermediate amount of water. The N-free extract increases with an increase in the amount of water; this variation is regular, with one exception. As in the case of corn, increasing the water applied to oats, decreases the per cent. of protein, and increases the ether extract and N-free extract.

WHEAT KERNELS.

The variety of wheat used was "New Zealand." It was planted on April 13th, and harvested on July 29th and 30th and August 5th. Table V shows the results obtained from the chemical analysis of the wheat kernels from the different plats.

TABLE V.—PERCENTAGE COMPOSITION OF WHEAT KERNELS.

Irrigation water applied. Inches.	Water in fresh substance.	In water-free substance.				
		Ash.	Protein.	Ether extract.	Crude fiber.	N-free extract.
4.63	7.70	2.70	26.72	2.37	5.44	62.77
5.14	8.16	3.32	25.11	5.24	3.05	63.28
8.81	8.25	2.96	21.25	3.63	4.38	67.75
10.30	8.47	2.54	19.93	2.09	4.47	70.97
12.36	8.14	3.12	22.18	2.12	4.31	68.27
17.50	7.59	2.79	18.57	2.34	5.88	70.43
21.11	6.80	2.50	16.99	1.97	3.92	74.62
30.00	8.70	4.50	15.26	1.85	3.19	75.20
40.00	8.01	2.72	18.43	1.94	3.42	73.48

There seems to be no regular variation in the per cent. of water, held by the fresh substance, to correspond with the amounts of water applied to the soil; neither does the per cent. of ash show any definite connection with the soil water. The per cent. of protein increases very markedly in the wheat kernel as the amount of water applied to the soil decreases. The plat that received 30 inches of water yielded wheat containing 15.26 per cent. protein, while the wheat from the plat that received 7.70 inches, contained 26.72 per cent.—a difference of 11.46. It is to be noted that the variation did not follow regularly the amounts of water used.

The variation in the ether extract are very irregular. The kernels raised with 5 to 8 inches of water contain the highest per cents. of fat. The crude fiber is not strongly affected by the soil water, though the tendency is for the per cent. to decrease as the amount of soil water increases. The per cent. of N-free

extract is highest in the wheat from the plats that received most water. As with corn and oats, increased watering of wheat decreases the per cent. of protein, and increases the per cents. of ether extract and N-free extracts.

POTATO TUBERS.

The variety of potatoes known as "Early Rose" was used in this experiment. They were planted on May 1st and 7th, and were dug on October 22d. They were immediately sampled and subjected to chemical analysis. Traces of reducing sugar were found in all the samples, and a trace of sucrose in one sample. The quantitative determinations are exhibited in Table VI.

TABLE VI.—PERCENTAGE COMPOSITION OF POTATOES.

Irrigation water applied. Inches.	Water in fresh substance.	In water-free substance.						
		Ash.	Protein.	Ether extract.	Crude fiber.	Starch.	Undeter- mined.	N-free extract.
8.08	76.00	6.68	11.83	0.55	2.69	69.95	8.30	78.25
10.00	76.34	4.57	12.57	0.11	2.46	69.55	10.74	80.29
15.00	75.54	4.85	12.52	0.33	2.21	72.58	7.50	80.08
20.00	76.24	4.29	11.46	0.50	2.56	76.25	4.94	81.19
27.00	75.95	4.99	10.77	0.06	1.93	75.10	7.15	82.25
39.99	76.00	4.87	8.33	0.79	2.06	76.48	7.47	83.95

It is quite noteworthy that the variation in the amount of moisture in the fresh potatoes is very small. In fact, the soil moisture seems to have little, if any, effect on the water content of potatoes. The per cent. of ash does not vary with the amount of water applied. As in the case of the grains, the relative amount of protein becomes larger as the irrigation becomes smaller. The one exception to this rule is the plat which received least water. The difference between the maximum and minimum per cents. is 4.24—sufficient to affect, materially, the food value of the potatoes. The variation of the ether extract is very irregular and does not follow the variation in the amount of water applied to the soil. The crude fiber shows a tendency to decrease on the well-watered plats. The per cent. of starch, on the other hand, increases very regularly with the increased irrigation. The difference between the highest and lowest per cents. of starch is 6.93—also quite sufficient to affect the food value of the tubers. The undetermined portion does not vary regularly with the soil moisture, but there appears to be a tendency for it to decrease as the watering becomes more liberal.

SUGAR-BEETS.

The German Kleinwanzlebener seed was used in these investigations. Seeding was done on April 25th and 26th. The beets were harvested on October 22d. The composition of the beets on the date of harvesting is shown in Table VII.

TABLE VII.—PERCENTAGE COMPOSITION OF SUGAR-BEETS.

Irrigation water applied, inches.	Water in fresh sub- stance.	In water-free substance.							
		Ash.	Protein.	Ether extract.	Crude fiber.	Reducing sugars.	Sucrose.	Starch.	N-free extract.
12.32	76.23	4.76	9.68	0.29	5.37	1.22	60.85	6.33	79.91
15.57	75.95	5.14	8.15	0.31	5.24	1.17	63.20	6.33	81.13
17.64	75.34	4.38	10.51	0.32	4.80	1.24	61.62	6.19	80.01
20.06	76.46	4.89	10.42	0.36	5.06	0.94	60.83	6.91	79.27
21.00	78.67	4.98	7.50	0.18	6.02	1.53	57.21	7.46	81.32
25.31	75.69	4.69	8.98	0.36	4.98	0.64	62.93	7.10	80.80
40.82	77.58	4.69	5.63	0.45	5.68	1.18	62.01	7.05	83.55
53.96	73.39	3.79	6.10	0.36	4.79	1.89	60.65	7.07	84.96

The per cent. of water in the fresh substance does not vary, in general, with the variation in soil moisture. The per cent. of ash is irregular and does not follow the soil moisture. The per cent. of protein tends to increase with increased applications of water, until 20 inches have been applied; from then on there is a distinct decrease. The difference between the highest and lowest per cent. is 2.92. The per cents. of ether extract, crude fiber and reducing sugars are so irregular that they cannot well be connected with the variation in the soil moisture. The sucrose, which is the most important constituent of the sugar-beet, constitutes from 57.21 per cent. to 63.20 per cent. of the water-free substance. Regular changes in the soil moisture do not seem to cause corresponding regular variations in the sucrose content. This is surprising, in view of the comparative regularity with which the nitrogen-free extract in the crops, previously studied, has increased with the increase in soil moisture. The per cent. of starch increases somewhat with the increase in soil moisture.

From these data, it would seem that the relative proportions of the constituents are not markedly affected by variations in soil moisture. The great regularity in variation that has prevailed

in other crops leads to some doubt concerning the correctness of this view. The plats on which the sugar-beets were grown were very different in depth and in the proportion of gravel, and they had been manured differently. Further, the accurate sampling of beets is a matter of great difficulty. It must also be remarked that the beet was dried and ground before analysis, which is not the best method to be followed in making carbohydrate determinations in sugar-beets. While the per cent. of total carbohydrates may be very near the truth, the sucrose and other single constituents may have suffered change during the process of drying. These questions must be left, however, for future investigations.

To obtain fuller and more accurate data on the effect of soil moisture upon the sugar content and purity of the juice, the plats were sampled and the beets analyzed weekly, from August 19th to October 16th. The average results for the sugar in the juice are found in Table VIII.

TABLE VIII.—PER CENT. OF SUCROSE IN THE JUICE FROM SUGAR-BEETS.

Irrigation water applied. Inches.	August 19th to September 3rd.	September 10th to September 25th.	October 2nd to October 16th.
11.16 to 17.78	11.35	13.14	14.83
19.95 to 26.66	12.58	13.72	15.86
40.82 to 53.96	13.40	14.62	15.25

It is quite evident, from the above table, that during the first two periods, the per cent. of sugar in the juice increases with the increase in the amount of water applied. During the last period, the beets grown with more than 40 inches of water contain 0.61 per cent. less sugar than do those grown with an average of 23.31 inches of water. The general conclusion to be drawn from this table is, that increasing the soil moisture tends to increase the per cent. of sugar in the juice of sugar-beets.

TABLE IX.—PER CENT. PURITY IN JUICE FROM SUGAR-BEETS.

Irrigation water applied. Inches.	August 19th to September 3rd.	September 10th to September 25th.	October 2nd to October 16th.
11.16 to 17.78	77.0	77.9	81.1
19.95 to 26.66	80.6	81.1	82.7
40.82 to 53.96	80.5	82.7	84.2

Table IX shows very clearly that the purity of the juice is highest with sugar-beets grown with large amounts of water but that the differences are so small as to have little practical value.

DISCUSSION.

A study of the preceding tables confirms the belief that the soil moisture influences strongly the chemical composition of plants and plant parts. To what extent the compositions of different plants and plant parts are affected by soil moisture, cannot, of course, be determined from this preliminary investigation. However, it may safely be concluded that the protein and nitrogen-free extract are influenced more than any other chemical group contained by plants. It may further be concluded that withholding water from the plant increases the per cent. of protein, and diminishes the per cents. of nitrogen-free extract and fat; increasing the supply of water decreases the per cent. of protein and increases the per cents. of nitrogen-free extract and fat.

That the variation is far greater than that ordinarily assumed to be possible is shown by Table X, in which the differences between the lowest and highest per cents. of protein, fat, nitrogen-free extract and starch are given, due regard having been had for the variation due to the application of different amounts of water.

TABLE X.—DIFFERENCE BETWEEN HIGHEST AND LOWEST PER CENTS.
DUE TO VARYING SOIL MOISTURE

Substance.	Protein.	Fat.	N-free extract.	Starch.
Corn kernels.....	2.56	0.90	2.33	...
Oat kernels.....	5.31	0.68	1.69	...
Wheat kernels.....	11.46	1.78	12.43	...
Potatoes.....	4.24	...	5.70	6.93
Sugar-beets.....	4.88	...	5.05	...

While the power to control the composition of plants by varying the soil moisture is of immense practical value to all irrigated countries, yet its higher theoretical importance must not be overlooked. To the plant physiologist it opens a large field of research, which promises to result in light being thrown on some of the obscure parts of our knowledge of plant growth and plant life. The temptation to theorize, even with the meager data of this paper, is very great, but as considerable material on this subject has been gathered since 1901, the discussion of the physiological relations of the data, here presented, has been left for future reports. However, it may be said that the soil moisture is only one of many factors controlling the composition of

plants, and that the great variations, recorded in this paper, were partly due to the peculiar soil conditions prevailing on the Station farm.

This investigation has been continued since 1901, and is still being continued.

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[CONTRIBUTION FROM THE NEW YORK AGRICULTURAL EXPERIMENT
STATION.]

RENNET ENZYME AS A CAUSE OF CHEMICAL CHANGES IN THE PROTEIDS OF MILK AND CHEESE.

BY L. L. VAN SLYKE, H. A. HARDING AND E. B. HART.

Received September 23, 1903.

INTRODUCTION.

THE object of the work described in this article was, primarily, to ascertain to what extent the proteolytic phenomena, observed in cheese-ripening, are due to the action of an enzyme contained in the rennet extract used in cheese-making. It was also our purpose to learn how the proteolytic action of rennet compares with that of commercial pepsin.

It has been quite generally believed that the rennet extracts used in the manufacture of cheese contain not less than two enzymes or ferments, called rennin and pepsin, one ferment coagulating milk-casein and the other converting milk-casein and paracasein, under favorable conditions, into soluble forms of nitrogen compounds. The present tendency, however, is in the direction of the belief that both kinds of action are due to the presence of only one enzyme. The presence of a proteolytic ferment in rennet extract is readily understood, when we consider its source, which is the stomach of a suckling calf.

For years the weight of opinion was against the belief that rennet has any other function in cheese-making than simply to coagulate milk-casein. In some work¹ done by one of us in 1892, it was shown that cheese, made with larger amounts of rennet, furnished greater quantities of soluble nitrogen com-

¹ New York Agr. Expt. Sta. Bull. No. 54, p. 267 (1893).

pounds than did cheese made with smaller amounts of rennet. In 1899, some additional work¹ was done, confirming the results previously obtained. Babcock, Russell and Vivian² have made a very thorough investigation of this subject, showing that, in the case of normal cheese, increased use of rennet resulted in a more rapid increase of soluble nitrogen compounds, especially of those nitrogen compounds grouped under the names of caseoses and peptones. They also made cheese from milk to which purified commercial pepsin had been added and found similar chemical changes taking place in the cheese thus made. They concluded, from these experiments with normal cheese, that rennet exerts a digestive influence on casein, due to the presence of peptic enzymes contained in rennet extracts, the action of which is intensified by the development of acid in the cheese-curd. Jensen,³ working independently and along quite different lines, reached the same conclusions at the same time.

In the case of the work previously done here and elsewhere, the effect of rennet ferment has not been studied apart from the action of other factors that are present in normal cheese-ripening. So far as our present knowledge goes, the different agencies taking part in the normal process of cheese-ripening are the following: (1) Some acid, usually lactic; (2) enzymes present in the milk before it is made into cheese; (3) an enzyme contained in the rennet extract added to milk in the cheese-making process; and (4) micro-organisms, chiefly bacteria. In previous studies of the effect of rennet ferment on cheese-ripening some or all of these factors have been present, so that the specific action of rennet has had to be inferred rather than been clearly proved. It has been the special aim of our work to study the action of the rennet ferment as far as possible apart from the other agencies of cheese-ripening. Under these conditions, we have studied the action of rennet extracts in cheese-ripening: (1) Without acid, (2) in the presence of acid, (3) without salt, and (4) with salt. In addition, we have studied the action of rennet extracts of different ages upon the casein of milk, and also the proteolytic action of commercial pepsin on milk-casein and in the process of cheese-ripening. We have also studied the action of rennet enzyme and pepsin on paracasein dilactate.

¹ New York Agr. Expt. Sta. Bull., No. 236, p. 150 (1903).

² Annual Report, Wis. Expt. Sta., 17, 102 (1900).

³ *Landw. Jahrb. d. Schweiz.*, 14, 197 (1900).

DESCRIPTION OF EXPERIMENTAL WORK.

DIFFICULTIES INVOLVED IN THE WORK.

In order to destroy all enzymes present in milk, our general plan of procedure has been to heat the milk to a temperature varying in different cases from 85° C. to 98° C. (185° F. to 208° F.). Then, in order to prevent possible contamination by the entrance of enzyme-producing organisms, the milk, after being heated and cooled, has been treated with 3 to 5 per cent. of chloroform by volume, previous to being made into cheese. The heating of milk to the temperature stated diminishes the readiness and completeness with which it is coagulated by rennet extract, but the power of prompt coagulation by rennet can be restored by the addition of calcium chloride or carbon dioxide or any ordinary acid. In thus eliminating other factors of cheese-ripening than rennet enzyme, we necessarily produce conditions that do not exist in normal cheese-making, such as (1) heated milk, (2) absence of milk-enzymes, (3) the use of calcium chloride or carbon dioxide, and (4) absence of enzyme-forming and acid-forming organisms. In a study carried on under such conditions, we cannot expect our results to be entirely comparable with results obtained under normal conditions; but we can secure data that enable us to determine the ability of the rennet enzyme to cause proteolytic changes under the conditions of experiment employed. Later we will inquire as to whether the introduction of such unusual conditions seriously affected the value of the results obtained, in their application to the process of normal cheese-ripening.

EFFECT OF ACID UPON THE PROTEOLYTIC ACTION OF RENNET ENZYME.

Table I contains the averages of results given by four sets of experiments, in which the effect of the presence and absence of acid upon the action of rennet enzyme in cheese-ripening was studied.

TABLE I.—EFFECT OF PRESENCE AND ABSENCE OF ACID UPON THE ACTION OF RENNET ENZYMES.

		Nitrogen, expressed as percentage of nitrogen in cheese, in form of			
Acid.	Age of cheese when analyzed.	Water-soluble nitrogen compounds.	Paracasein monolactate.	Paranuclein caseoses and peptones.	Amides.
		Per cent.	Per cent.	Per cent.	Per cent.
Present	Fresh	4.55	26.80	3.78	0.77
"	12 mos.	25.85	11.59	20.87	4.98
Absent	Fresh	3.13	1.88	2.73	0.80
"	12 mos.	4.23	1.68	2.26	3.96

A comparison of the data embodied in this table shows a relatively large formation of water-soluble nitrogen compounds in twelve months in the presence of acid, while in the absence of acid practically no proteolysis had occurred. Paracasein monolactate was present in only minute quantities, if at all, in the absence of acid, while a considerable amount was formed in the presence of acid. The increase of soluble nitrogen compounds was confined largely to the paranuclein, caseoses and peptones, the amount of amides remaining small. In normal cheese-ripening, we find these relations reversed, that is, the amides form a considerably larger part of the soluble nitrogen compounds than do the higher groups.

The results embodied in Table I may properly be interpreted as showing that the proteolytic action of the rennet enzyme, in cheese-ripening, is dependent upon the presence of acid.

EFFECT OF RENNET ENZYMES IN CHEESE CONTAINING ACID-FORMING AND SOME PROTEOLYTIC ORGANISMS.

For the purpose of comparison, it was desired to have some cheeses made from milk pasteurized at 85° C. (185° F.). As factors active in causing proteolytic changes, we had in the cheeses made in these experiments (1) acid, (2) rennet enzyme, and (3) such micro-organisms as happened to be introduced with the "starter" and from the air of the room. As compared with a normal cheese, there were no milk enzymes present and the biological factor would be expected to be considerably less marked. In comparison with the cheeses referred to in Table I, we had in these no chloroform, a difference that meant absence of a biological factor in the former case. In these cheeses, the acid was furnished by a sour-milk "starter." In Table II, we give the results of chemical analysis made when the cheese was fresh from the press and when nine months old.

TABLE II.—SHOWING COMPOSITION OF CHEESE MADE FROM PASTEURIZED MILK.

Age of cheese when analyzed.	Nitrogen, expressed in percentage of nitrogen in cheese, in form of				
	Water-soluble nitrogen compounds. Per cent.	Para- casein mono- lactate. Per cent.	Paranuclein, caseoses and peptones. Per cent.	Amides. Per cent.	Am- monia. Per cent.
Fresh	3.13	11.36	3.13	0	0
9 months.....	25.54	5.14	12.79	12.75	1.31

In studying these results, we notice that there was an increase in all the different classes of water-soluble compounds during the period of experiment. The amount of amido compounds was considerably in excess of that noticed in Table I in the case of cheeses made and kept in the presence of chloroform. Ammonia was formed, while none was present in Table I. The increased amounts of amido compounds and the presence of ammonia, observed in these experiments, as compared with the results of the experiments given in Table I, must be ascribed to the presence in the former of a biological factor and not to rennet enzyme.

COMPARISON OF THE EFFECT OF COMMERCIAL PEPSIN WITH THAT OF RENNET ENZYME IN CHEESE-RIPENING.

In the following experiments, the cheeses were made in the normal way, without chloroform, except that the milk was pasteurized at 85° C. (185° F.) and hydrochloric acid was used in the place of lactic acid or a "starter." In 55, rennet extract alone was used at the usual rate of 2.5 ounces for 1000 pounds of milk. In 56, in addition to rennet extract, we added 1 gram of Parke, Davis & Co.'s aseptic scale pepsin dissolved in water, and in 57, we used 15 grams of the pepsin and the usual amount of rennet extract.

TABLE III.—SHOWING EFFECT OF COMMERCIAL PEPSIN IN CHEESE-RIPENING.

No. of experiment.	Age of cheese when analysed.	Enzymes added.	Nitrogen, expressed as percentage of nitrogen in cheese, in form of				
			Water-soluble nitrogen compounds. Per cent.	Paracasein monolactate. Per cent.	Paracasein, casein and pepsin. Per cent.	Amides. Per cent.	Ammonia. Per cent.
55	Fresh	Rennet	4.76	65.45	2.41	2.36	0.0
55	6 mos.	extract	28.37	17.14	15.87	6.35	2.00
56	Fresh	Rennet and	6.97	36.76	4.11	2.86	0.0
		1 gram					
56	6 mos.	pepsin	29.80	17.04	16.47	7.10	1.91
57	Fresh	Rennet and	25.00	59.53	22.80	2.20	0.0
		15 grams					
57	3 mos.	pepsin	46.67	11.61	41.00	5.68	0.49

In studying the results contained in Table III, we notice:

(1) The use of 1 gram of commercial pepsin in addition to rennet extract slightly increased the proteolytic results in the cheese. This cheese contained considerably less moisture than 55 or 57.

(2) The use of 15 grams of commercial pepsin along with rennet extract produced very marked results. This is strikingly evident in the fresh cheese, where we have 25 per cent. of the nitrogen in the cheese present in the form of water-soluble compounds, while in the case of Experiment 55, in which rennet extract only was used, the amount of soluble nitrogen compounds is less than 5 per cent. At the end of three months, we still have much more of the soluble nitrogen compounds in 57, the pepsin cheese, than we have in 55, the rennet extract cheese, at the end of six months.

(3) In comparing the proteolytic factors in Experiments 55 and 57, the conditions of work were such that the chief essential difference was the presence of pepsin in the latter, though 57 contained more moisture than 55. The observed difference in the chemical results could, therefore, be due only to pepsin, and this would be particularly true of the results obtained in the fresh cheese.

COMPARISON OF THE EFFECT OF RENNET ENZYME AND OF COMMERCIAL PEPSIN IN MILK, WITH AND WITHOUT ACID.

We made a comparative study of the effect of rennet enzyme and of commercial pepsin upon milk-casein and upon casein monolactate. These experiments were carried out in the following manner: We heated 8.6 liters of milk for fifteen minutes at 85° C. (185° F.), and after cooling added 2 per cent. of chloroform by volume. Of this milk, we placed in each of several bottles 100 cc. In one case, we added, to the neutral milk, 0.22 cc. of Hansen's fresh rennet extract, and in another the same amount of old rennet extract. In other bottles, we added, in addition to the rennet extract, 0.5 cc. of pure concentrated lactic acid, which was sufficient to convert the milk-casein into the monolactate. For comparison, we placed in other bottles, with and without acid, the same amount of milk and 0.06 gram of Parke, Davis & Co.'s aseptic scale pepsin for each 7 grams of proteid contained in the milk. Duplicates were used in all cases. The

contents of these bottles were kept at 15.5° C. (60° F.) and were examined at intervals, both chemically and bacteriologically. With the exception of a single determination, in the case of one bottle, the germ content was below 50 per cubic centimeter, which undoubtedly represented spore forms. The old rennet extract was used for the purpose of answering the question as to whether the proteolytic changes, observed in Table I, were due to rennet enzyme alone, or whether the rennet may not have contained some proteolytic bacterial enzymes produced in the rennet extract previous to its use.

The results of chemical analysis are given in the subjoined table. The determinations of nitrogen in the form of amides were made by the use of phosphotungstic acid, since it has been shown¹ that, in the case of peptic digestion, phosphotungstic acid is a more satisfactory reagent than tannic acid, especially in solutions having an acid reaction. The amount of nitrogen originally in the milk was 0.561 per cent.

TABLE IV.—SHOWING THE EFFECT OF RENNET ENZYME AND COMMERCIAL PEPSIN UPON MILK-CASEIN AND CASEIN MONOLACTATE.

Kind of enzyme used.	With or without lactic acid.	Age of milk when analyzed.	Nitrogen, expressed as percentage of nitrogen in milk, in form of		
			Soluble nitrogen compounds. Per cent.	Caseoses and peptones. Per cent.	Amides. Per cent.
.....	Fresh	9.98
Fresh rennet	Without	1 mo.	11.35	6.00	5.35
" "	With	1 "	29.80	22.22	7.58
Old rennet	Without	1 "	12.57	4.99	7.58
" "	With	1 "	25.23	18.55	6.68
Commercial pepsin	Without	1 "	8.91	2.22	6.69
" "	With	1 "	33.51	25.93	7.58
Fresh rennet	Without	9 mos.	18.98	13.63	5.35
" "	With	9 "	53.57	45.64	7.93
Old rennet	Without	9 "	17.03	12.13	4.90
" "	With	9 "	47.96	39.67	8.29
Commercial pepsin	Without	9 "	10.08	6.51	3.57
" "	With	9 "	56.96	48.05	8.91

The data embodied in Table IV appear to be quite definite in respect to the following points:

(1) The increased activity of rennet extract as well as of pepsin in the presence of acid is very marked. Expressed in another

¹ New York Agr. Expt. Sta. Bull. No. 215, pp. 90 and 98 (1900).

way, these enzymes act upon casein monolactate much more extensively than upon milk-casein.

(2) If we compare the results secured by the use of the purest commercial pepsin with those given by the rennet extracts, we find that, in the presence of acid, there are formed soluble nitrogen compounds quite close in amount to those formed by rennet extract. The amount of soluble nitrogen compounds formed in neutral solution was fairly stationary during the nine months, while, in the case of the rennet extracts, there was a slow increase. The amount of amido compounds was surprisingly uniform in the case of the pepsin and the rennet extracts, in both neutral and acid reaction.

(3) At any given time, the fresh rennet extract had, in most cases, formed a larger amount of soluble nitrogen compounds than had the old extract. This was particularly true in acid solution. This result does not indicate that we had bacterial enzymes in the old rennet in addition to rennet enzyme. The difference in action of the two rennet extracts is not marked in the class of amido compounds. If the old extract contained bacterial enzymes, we should expect it to produce larger amounts of amido compounds. These results fail to show that the old rennet extract contained any proteolytic bacterial enzymes, as compared with the fresh extract. Moreover, the results given by pepsin suggest that the pepsin was able to account for all the changes observed in the case of the rennet extracts in the presence of acid.

COMPARISON OF THE EFFECT OF RENNET ENZYME AND OF COMMERCIAL PEPSIN ON PARACASEIN DILACTATE.

Paracasein monolactate was extracted from several pounds of cheese by a 10 per cent. solution of sodium chloride and this was treated with acid, precipitating paracasein dilactate. Of this compound washed free from salt, we placed 25 grams, suspended in water, in each of several flasks and sterilized by heat. We then sterilized some solution of pepsin and rennet extract by treating with 0.5 per cent. of formalin, containing 0.2 per cent. of formaldehyde. According to Bliss and Novy,¹ pepsin is not affected by a 1 per cent. solution of formaldehyde nor rennet by a 4 per cent. solution. In one set of flasks, we added to each

¹ *Jour. Expt. Med.*, 4, No. 1 (1899).

0.06 gram of the sterilized pepsin, and in each of the other set of flasks 0.5 cc. of the sterilized rennet extract. Duplicates were used in all cases. These were examined bacteriologically and chemically, at intervals for three months. The formalin was very effective in destroying bacterial forms. In some cases a few molds were found, but not in sufficient number to affect the work. The nitrogen in the material was 4.35 per cent.

TABLE V.—SHOWING EFFECT OF RENNET ENZYME AND COMMERCIAL PEPSIN ON PARACASEIN DILACTATE.

Enzymes used.	Age when analysed.	Nitrogen, expressed as percentage of nitrogen in mixture, in form of				
		Water-soluble nitrogen compounds Per cent.	Para-casein mono-lactate. Per cent.	Para-nuclein caseoses and peptones. Per cent.	Amides. Per cent.	Ammonia. Per cent.
Pepsin	2 weeks	33.68	2.30	0
Rennet	"	34.95	2.30	0
Pepsin	1 mo.	41.61	...	37.87	3.74	0
Rennet	"	43.68	...	40.00	3.68	0
Pepsin	3 "	55.75	...	46.55	9.20	0
Rennet	"	57.25	...	49.53	7.72	0

From the data contained in Table V, we can see that the results of our work indicate that:

(1) Both pepsin and rennet enzyme exerted a marked proteolytic effect upon the paracasein dilactate, digesting about one-third of it in two weeks and considerably over one-half in three months. While the rennet enzyme appears somewhat more active in forming water-soluble nitrogen compounds, the actual difference is small.

(2) Both enzymes formed amides in small quantities, but neither produced any ammonia.

(3) If we compare the results in Table V with those in Table III, we find that more proteolysis occurred in this experiment than in the presence of chloroform. This is true of both enzymes. This suggests that the chloroform may exert a retarding influence upon the action of pepsin and rennet. Malfitano¹ makes the statement that the action of pepsin is considerably diminished by chloroform. The difference noted in our work may be due to the greater amount of acid present in the experiment in Table V. However, both sets of experiments practically agree in showing small formation of amides and entire absence of ammonia.

¹ *Ann. Inst. Pasteur*, 16, 853 (1902).

EFFECT OF COMMON SALT ON THE ACTION OF RENNET ENZYME IN CHEESE-RIPENING.

Previous work¹ shows that salt exerts a marked repressing influence upon the proteolytic action of those enzymes that are present in milk when made into cheese. We have also found that in normal cheese the addition of increased quantities of salt decreases the rapidity of proteolysis. We planned several of our experiments with a view to study the action of salt on cheese-ripening, when rennet enzyme is the only proteolytic factor present. The results were not at all conclusive, but seem to indicate, as far as they go, that, in cheese-ripening, salt, in the proportions commonly used, has little or no influence upon the action of rennet enzyme. It may be mentioned, in this connection, that Chittenden and Allen² have shown that the action of pepsin, in digesting blood-fibrin, is diminished by the presence of common salt.

EFFECT OF ABNORMAL CONDITIONS PRESENT.

We have already called attention to the difference of conditions present in the experiments described in this bulletin and those found in normal cheese. We will now consider these in more detail. These abnormal conditions, found in our experiments, but not present in normal cheese, are the following: (1) Milk heated to 85° C. to 98° C. (185° F. to 208° F.) to destroy all enzymes originally existing in milk; (2) the use of calcium chloride or carbon dioxide gas to restore the coagulating property of milk-casein by rennet extract; and (3) the use of chloroform to suppress all activity of organisms. The question naturally arises as to whether the introduction of these unusual conditions seriously affected the results obtained and, if so, in what manner and to what extent.

If the conditions mentioned showed any influence upon the action of rennet enzyme, the tendency was an unfavorable one for the action of this enzyme.

SUMMARY AND DISCUSSION OF RESULTS.

In the work described in the preceding pages, we have studied the proteolytic action of rennet enzyme under the following conditions:

¹ New York Agr. Expt. Sta. Bull. No. 203, p. 241 (1901).

² "Studies in Physiological Chemistry," Yale Univ., I, 92 (1884-'85).

(1) *In Cheese Containing Rennet Enzyme as the Only Proteolytic Agent, with and without Acid, and also with and without Salt.*—In these experiments, all milk-enzymes were destroyed by heating at 95° C. to 98° C. (205° F. to 208° F.); the coagulable property of the milk-casein was restored by the addition of either calcium chloride or carbon dioxide gas, and all organisms were rendered inactive by chloroform. Acid, when present, was furnished by addition of pure lactic acid.

(2) *In Cheese Containing Rennet Enzyme together with Acid-forming and Some Proteolytic Organisms.*—In these experiments, the milk-enzymes were destroyed by heating, acid was furnished by a lactic acid "starter," but no chloroform was used. We thus had, as our only proteolytic agents, rennet enzyme in the presence of acid and some liquefying organisms that were introduced in the "starter" or that got into the milk or curd during the operation of cheese-making.

(3) *In Cheese Containing Commercial Pepsin in Addition to Rennet Enzyme, together with Hydrochloric Acid and Such Organisms as Were Introduced during the Process of Making Cheese.*—In these experiments, the milk enzymes were destroyed by heat and commercial pepsin added in different amounts.

(4) *In Comparison with Commercial Pepsin on Casein in Milk, with and without Acid.*—In these experiments, the milk enzymes were destroyed by heat and all organisms were rendered inactive by chloroform.

(5) *In Comparison with Commercial Pepsin on Paracasein Dilactate.*—In these experiments, rennet enzyme and commercial pepsin, sterilized by formaldehyde, were allowed to act upon sterile paracasein dilactate.

The results of these experiments appear to us to justify the following statements:

(1) In the case of every experiment made, whether with cheese or milk, there was little or no proteolytic action of either rennet enzyme or commercial pepsin in the absence of acid, while there was marked action, though in varying degrees, in the presence of acid.

(2) In the absence of acid in cheese, no paracasein lactate is formed and little or no proteolysis occurs; in the presence of acid in cheese, or more strictly in the milk and curd, paracasein mono-

lactate is formed and proteolysis takes place, with the rennet ferment as the active agent. The ability of rennet enzyme to convert paracasein into soluble nitrogen compounds appears to depend upon the presence of paracasein lactate. In cheese-making, therefore, the primary function of acid appears to be the formation of a chemical compound with paracasein, commonly paracasein monolactate but, in excess of acid, paracasein dilactate. The conversion of paracasein monolactate by rennet enzyme into soluble nitrogen compounds is strongly suggested by the fact that, when the soluble nitrogen compounds increase, the paracasein monolactate decreases.

(3) In comparing rennet enzyme and commercial pepsin in the case of cheese, milk and paracasein dilactate, the experiments that were strictly parallel have shown about the same extent of proteolytic action.

(4) In the case of both rennet enzyme and commercial pepsin, the chemical work performed by the ferments is confined mainly to the formation of paranuclein, caseoses and peptones, while only small amounts of amides are formed, and no ammonia.

(5) Rennet enzyme is a peptic ferment, as shown by the following characteristics: (a) Neither rennet enzyme, nor pepsin causes much, if any, proteolytic change, except with the help of acid; (b) the quantitative results of proteolysis furnished by rennet enzyme and pepsin agree closely when working on the same material under comparable conditions; (c) the classes of soluble nitrogen compounds formed by the two enzymes are the same both qualitatively and quantitatively; (d) neither enzyme forms any considerable amount of amido compounds, and neither produces any ammonia; (e) the soluble nitrogen compounds formed by either enzyme are chiefly confined to the groups of compounds known as paranuclein, caseoses and peptones.

(6) The experiments made to determine the influence of salt on the proteolytic action of rennet enzyme, while not conclusive, suggest that salt has little or no effect upon the action of rennet enzyme in cheese-ripening.

(7) In obtaining our results relating to the study of the function of rennet enzyme in cheese-ripening, we were necessarily compelled to work under conditions more or less abnormal as compared with the conditions commonly present in cheese-

making. The effect of such unusual conditions would tend, if they had influence at all, to diminish the proteolytic action of rennet enzyme. We are, therefore, justified in believing that our results represent the minimum effect of rennet enzyme in cheese-ripening and that, under normal conditions, it takes, if anything, a larger part than that indicated by our experiments.

(8) In some experiments, we eliminated all milk enzymes and all active forms of organisms contained in the milk before making it into cheese. In some cases, we had rennet enzyme in the presence of acid as the only proteolytic agent in the cheese; in others, we had the same conditions and, in addition, such proteolytic organisms as chanted to get into the milk and curd during the process of cheese-making. In the latter case larger amounts of amides were formed, and some ammonia, while, in the presence of rennet enzymes alone, no ammonia was formed and only small amounts of amido compounds. When we compare normal cheese with cheese containing only rennet-enzyme, we find the same difference, except that it is more pronounced, as we should expect. Hence, the special work done by the rennet enzyme as a factor in cheese-ripening is that of a peptic digestion, forming groups of water-soluble nitrogen compounds, intermediate in complexity of structure between paracasein and the amido compounds, *viz.*, paranuclein, caseoses and peptones.

In normal cheese, we find an accumulation of amides and ammonia, as the cheese grows older, and a corresponding diminution of the compounds previously formed. The formation of all the ammonia and of a large proportion of the amides found in ripened cheese must be due to some agency other than rennet enzyme, and the only other agents present, besides milk enzymes, that can do this work appear to be organisms or their enzymes. The first stage in normal cheese-ripening is essentially a peptic digestion of paracasein monolactate. Gradually amides are formed and later ammonia. It is probable that the first chemical work done in normal cheese-ripening is the conversion of paracasein monolactate by rennet enzyme into paranuclein, caseoses and peptones. The question naturally arises as to whether these compounds must be formed before other agents can take part in the work and carry it along farther, producing amides and ammonia. We are at present engaged in studying this phase of the problem.

(9) When rennet enzyme was the only digesting agent in cheese, we were unable, in any case, to find the slightest traces of cheese flavor. Apparently, we must look to other sources for this important product of cheese-ripening.

NEW YORK AGRICULTURAL EXPERIMENT
STATION, GENEVA N. Y.

A METHOD OF GRADING SOAPS AS TO THEIR DETERGENT POWER.

BY H. W. HILLYER.

Received October 7, 1903.

AS FAR as known to the writer, no method for directly determining the detergent value of a soap is now known. It is assumed, and with much justice, that the value of a soap is a function of the amount of combined fatty acids present, and the valuation of soaps is now based on the determination of the fatty acids. Besides this, the determination of the free alkali and of water and various filling materials is required. These determinations give evidence on which the valuation of the soap may be based and, to some extent, for ascertaining the materials from which it is made, but do not give any direct measure of the value as a cleansing agent and, further, require a complex judgment to interpret them.

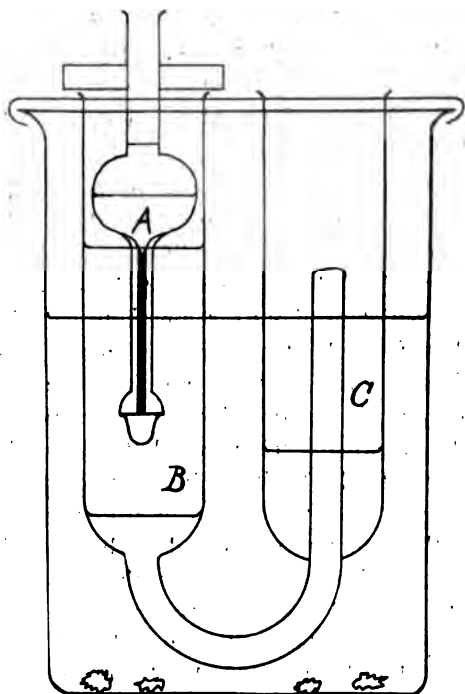
The method now proposed is based on the study of sodium soaps, previously published in this Journal, 25, 511 and 524. In the articles indicated, it was found that when a solution of a soap is made to form drops beneath the surface of an oil, the number of drops formed from a given volume of the solution is dependent on the amount of soap present in the solution. Further, the conclusion was reached that the number of drops formed was a measure of the emulsifying power of the given soap solution, and that the emulsifying power was so large a part of the cleansing power that it might stand as a measure of it, especially, since two of the other probable factors in cleansing, namely, penetrating or wetting power, and lubricating power are dependent on the same physical properties as the emulsifying power.

Soaps are used principally in one of two ways. They are used with cold or luke-warm water, as in wool-scouring and for toilet purposes; or, on the other hand, they are used in boiling water, as in silk-boiling, dish-washing, and laundry work. A soap may be of value for one of these purposes and of comparatively little value for the other. The method proposed takes these two peculiar conditions of use into account and attempts to grade the soaps as to their efficiency for cold use and, on the other hand, for use with hot water.

For making the test for efficiency in use with hot water, the apparatus is similar to that used for the study of sodium palmitate and stearate, but modified in the interest of greater constancy of results. The essential part is a pipette (A) with a capillary outlet of about 0.5 mm. internal diameter and a flat, horizontal surface, about 10 mm. in diameter, from which the drops fall. This surface must be free from capillary openings, which may contain air, as described in a former article. The reservoir of the pipette is spherical, that it may have a small vertical height relatively to its volume, since a great vertical height makes a greater difference in the pressure and consequent rate of flow at the commencement and at the end of an observation. When the initial pressure is great, the rapidity of flow may make the solution run down in a stream or cause the drops to be formed too rapidly to be easily counted. This may be overcome by dipping the pipette more deeply into the oil; but when that is done the later drops are formed more slowly than is desirable. By having the bulb capacious in proportion to its vertical height the initial and final rates of flow are nearly enough alike to prevent any special difficulty. The pipette holds 5 cc. from a mark on the stem to the upper end of the capillary. The stem has an internal diameter of 3 mm., wide enough to allow filling from above, and, to facilitate this method of filling, it is widened at the upper end into a small funnel.

The second part of the apparatus is the receptacle for the oil, which may be a simple test-tube, but is preferably made in the form (BC) indicated in the drawing. This form maintains a more nearly constant pressure and promotes more regular work. To maintain the apparatus at the boiling-point of water, it is supported in a large beaker, which is used as a water-bath. The

beaker is covered with a sheet of zinc or aluminum with its edges turned down over the edge of the beaker, and with a perforation cut in it suitable for the insertion of the apparatus.



To make use of the apparatus, 2 or 3 cc. of water are poured into B and then followed by 20 cc. of kerosene. A little of the solution to be tested, previously heated on a boiling water-bath, is poured into the pipette and shaken about, and then blown out through the capillary, using a piece of rubber tubing as a mouth-piece. This is repeated twice more. Then the pipette is filled full, and by a strong pressure from the lungs the air bubbles are forced out of the capillary and washed away. The pipette, supported in a cork, is placed in the kerosene, and the number of drops formed from 5 cc. of the solution is counted. The solution, as it flows from the pipette, falls to the bottom of the oil reservoir B and overflows into C, while the level of the kerosene remains constant and the variation of pressure is that only which results from the change of level of the solution in the pipette.

Since this is in every case the same, comparable results are more easily obtained than by the use of a test-tube as oil reservoir.

To make a test of efficiency of the soap for use in cold water, the same apparatus is used, except that the beaker, used as a water-jacket, is not necessary.

As a standard for the hot test, 1 gram of neutral sodium palmitate, dissolved in 200 cc. of hot water, is used. Of this, 10 cc., 20 cc., 30 cc., and 40 cc. are, respectively, diluted to 50 cc. with boiling water, giving solutions containing 0.2, 0.4, 0.6, and 0.8 of the standard. The number of drops formed by each of these solutions, when it flows into a kerosene, adopted as a standard kerosene, is determined, and also the number of drops formed by the standard solution itself and the number of drops formed by water. The data obtained are plotted as a curve in which the ordinates represent percentages of the standard and the abscissas represent the number of drops corresponding to the percentages of the standard. The data, obtained with a certain kerosene, are here given and the curve (A) derived is shown in the figure.

The standard is made by bringing together 0.921 gram of palmitic acid and 36 cc. decinormal sodium hydroxide and diluting to 200 cc. with hot water.

Full standard gives drops 271-265-269 = 268 average.

0.8 " " " 228-228 = 228 "

0.6 " " " 180-178 = 179 "

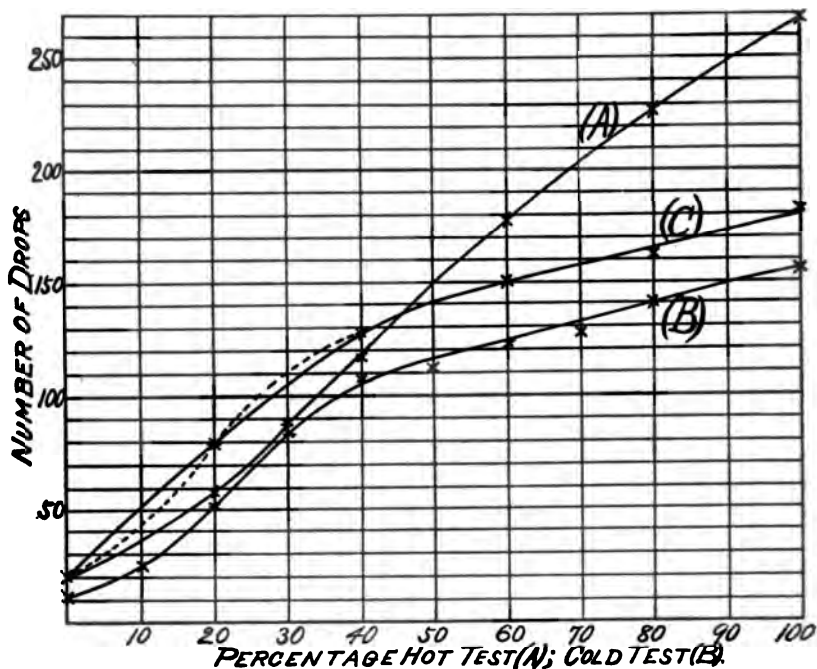
0.4 " " " 118-121 = 119 "

0.2 " " " 56-55½ = 56 "

Water " " " 19 = 19 "

If any solution of sodium palmitate, which contains an amount less than one part in 200 of water, is tested by the dropping method at the boiling-point, the amount present may be determined by counting the number of drops formed. By finding, on the curve, a point corresponding to the number of drops counted and letting fall a perpendicular from this point upon the base line, a point will be found which indicates, as a percentage of the standard, the amount of palmitate present.

Other soaps may be tested in the same way and referred to sodium palmitate as a standard. If 0.5 gram of a commercial soap is dissolved in 100 cc. hot water and its solution tested at the boiling-point, we may state the result in this way: The soap



in question gives the number of drops which would be given by a solution of sodium palmitate containing (x) per cent. of the standard.

According to the conclusions arrived at in the previous articles, the number of drops is a measure of the detergent power of the solution. Consequently, the result of the test may be stated as follows: The soap has, when used for cleansing with hot water, a detergent power as great as a soap containing (x) per cent. of sodium palmitate.

TEST FOR COLD-WATER SOAPS.

A solution containing one part of sodium oleate in 200 parts of cold, freshly boiled, distilled water is taken as the 100 per cent. standard for soaps to be used with cold water. From this, fractional standards are made as before, using cold, freshly boiled, distilled water to dilute with. All are tested as to their drop number in the cold and a curve constructed. In a previous article it was stated that the curve for sodium oleate was differ-

ent in shape from the curves for the other sodium soaps tested. The following data gives a curve for oleate (B), which appears to have nearly the same form as the curves previously given for rosin soap and different from the curves formerly given for oleate. But this difference is due to the greater dilution of the solution and to the greater number of fractional standards, and to the fact that observations are made nearer the origin. The curve shows that sodium oleate is somewhat hydrolyzed at great dilutions. A set of standards gave the following data and curve (B).

Full standard gives drops $153-153 = 153$ average.

0.8	"	"	"	$139-141 = 140$	"
0.7	"	"	"	$128-128 = 128$	"
0.6	"	"	"	$123-122 = 123$	"
0.5	"	"	"	$111-111 = 111$	"
0.4	"	"	"	$107-105 = 106$	"
0.3	"	"	"	$84 = 84$	"
0.2	"	"	"	$51-50 = 51$	"
0.1	"	"	"	$25-25 = 25$	"
Water	"	"	"	$11-11 = 11$	"

For evaluating a commercial soap for efficiency in use with cold water, the following method of working was decided upon after trying several others, which will be indicated later. The soap to be tested is shaved as thin as possible, and 0.5 gram of the shavings weighed and placed in a 100 cc. flask. The flask is then filled to the mark with cold, freshly boiled water and allowed to stand over night. In the morning the solution is stirred, and filtered through a dry filter, letting all run through that will and keeping the solution in the funnel protected from the carbon dioxide of the air by a watch-glass. When all has run through, the filtrate is stirred gently, avoiding making a foam, and a dropping test in the cold is made, using the same pipette and kerosene as that used in testing the standards. By applying, to the standard curve, the drop number observed, a number is obtained which may be stated, as in case of the hot test. A certain number of drops shows that the soap in question is as efficient for cold cleansing as an equal amount of soap containing (x) per cent. of sodium oleate.

Since surface-tension, viscosity, specific gravity and solubility, factors which enter more or less into the working of the test, are all influenced by changes of temperature, it is best to maintain

the temperature constant, as nearly as possible, in all the work involved in making the cold test. It will be convenient, in many cases, to select a convenient room temperature and maintain this, as nearly as possible, during the preparation and testing of the standards, and the preparation and testing of the soap solutions to be evaluated. If many tests are to be made, a trough with glass sides, through which a stream of hydrant water is maintained, might be convenient to set the flasks in and to receive the oil-holder while observations are being made.

Data obtained with a few commercial soaps are here given, showing for each the number of drops formed in the cold test and the percentage efficiency for cold use, indicated by the test; and the drop number by the hot test and percentage efficiency for hot use. The soaps tested are nearly all much-advertised soaps.

Number.	Cold.		Hot.		Remarks.
	Drops.	Efficiency.	Drops.	Efficiency.	
1	121	37	90	31	Cold made, cocoanut oil.
2	56	13	67	21	Hygienic cocoanut oil.
3	114	34	221	77	Toilet.
4	119	36	202	69	Shaving.
5	84	22	80	28	Tar, toilet.
6	75	19	103	35	Yellow laundry, rosin.
7	100	28	135	45	" " "
8	107	31	173	58	Household for cold use.
9	98	27	150	50	" " "
10	139	49	170	57	" " "
11	97	27	206	71	White laundry and toilet.
12	226	79	" "
13	216	75	Prime yellow laundry.
14	120	37	218	76	" " "
15	104	30	277	106	Steam laundry, tallow.
16	142	54	Castile, old and dry.

These results show how wide a difference there is between soaps which have wide sale and also the desirability of having some standard by which to readily judge them. In the retail market, many household soaps sell at the price of five cents per bar. The bars vary very much in weight, but it was found that in a number of cases the value per bar was approximately equal according to the dropping test. For example, No. 6 is sold in bars weighing 330 grams; its hot test shows 35 per cent. The product of these, or efficiency per bar is 115.5. No. 7 is sold in

270-gram bars. The hot test shows 45 per cent., or efficiency per bar, 121.5. No. 11 is sold in 160-gram bars. Hot test, 71 per cent. Efficiency per bar, 113.6.

This calculation shows that in some cases the manufacturers have correctly estimated the relative value of their product.

From the table it may be seen that those soaps intended for toilet purposes or advertised for cold use are, for the most part, of a relatively high efficiency by the cold test. No. 16 is a dry, old, standard castile soap and shows the highest cold test of any. But it is somewhat surprising that even this is only a little more than half as efficient as pure sodium oleate.

No. 15 is a soap known to be made from tallow. It is consumed by local steam laundries and regarded by them as the best soap they can find for their purpose. According to the hot test, it is above the standard palmitate in efficiency. Nos. 11, 12, 13, and 14 are among the most highly appreciated family soaps on the market, and show a high hot test.

That there is not a complete agreement between the tests and the advertised uses is not strong evidence against the test. The makers may be mistaken in their judgment of the best way to use their soaps, or they may, in some cases, purposely advertise them for uses to which they are not well adapted.

It is not expected that the method, at least in its present form, will give a very exact measure of the value of soaps, but it is hoped that, in a field where there is no exact method, the one here proposed may aid consumers in selecting soaps fitted to their special needs and in writing specifications by which soaps may be contracted for. It is also hoped that it may lead to a more concordant judgment, on the part of manufacturers, as to what a normal soap is, and as to how far it is legitimate to vary from this normal soap. If some ready method of judging a soap is adopted, it may seem unprofitable both to maker and consumer to pay freight charges on water and fillers which are of no real detergent value.

The hot test may be relied upon to give results concordant within 1 per cent. for successive samples and within a much closer limit in duplicate tests of the same sample. The cold test is not as accurate as the hot test on account of the colloidal

nature of the solution. It will probably grade soaps within 4 or 5 per cent. in the case of soaps whose solutions are very slimy, and within a closer limit in cases in which the solutions are mobile.

The working out of the hot test presented no particular difficulty, since the soaps worked with dissolve in hot water to give mobile solutions which readily flow through the pipette and can be readily duplicated. In working out the cold test, the method indicated was adopted only when other methods proved unsatisfactory. It is thought best to give an account of some of these attempts that others may not find it necessary to repeat them without modification.

At first the solutions, prepared for the hot test, were allowed to cool, then poured upon a filter and the filtrate tested cold. But the first portion of the filtrate gives a lower drop number than the later portions, and even if all is allowed to drain off before testing, and in this way an average for the whole sample obtained, the drop numbers for successive samples is not at all concordant. These difficulties are probably due to the great variation in the solubility of the colloidal precipitate which separates, with small differences in temperature and to the slowness with which equilibrium is reached between the dissolved and undissolved colloid.

It was thought that by making the solutions more dilute, they might have a low enough viscosity, when cold, to flow through the pipette without filtering. This was found to be the case when the solutions contained only one part in 400 parts of water but on testing several soaps of different classes in this way, they all showed nearly the same cold test and no comparison could be based on the results.

Another attempt was made by adding a solution of common salt to the soap solution and then filtering. It was found that when equal quantities of 2.5 per cent. sodium chloride solution were added to 0.5 per cent. sodium palmitate solution, that nearly all of the palmitate was precipitated and the filtrate showed only a small drop number. When the same salt solution was added to 0.5 per cent. oleate solution there was, at first, no precipitation and the drop number was *increased*. But the oleate solution with salt, on making successive tests, showed a rapidly decreasing drop number, making it impossible to use this mixture as a basis

for a standard curve. The decrease in number of drops is very soon apparent, the solution becomes cloudy, and, in a few days, nearly all of the oleate appears to be precipitated, while the filtrates, no matter what the original strength, show a strong tendency to the same minimum drop number.

LABORATORY OF ORGANIC CHEMISTRY,
UNIVERSITY OF WISCONSIN,
June, 1903.

A RAPID METHOD FOR THE DETERMINATION OF SULPHUR IN COAL AND COKE.

BY J. D. PENNOCK AND D. A. MORTON.

Received October 3, 1903.

As is well known, foundrymen require coke containing a minimum percentage of sulphur. It has been found necessary to be able to quickly determine the percentage of sulphur in the coal to be used for coke-making in order that a selection of those cars containing coal low in sulphur, may be made, for the railroad companies charge demurrage on all cars not emptied in twenty-four hours. By the method described in this paper, one chemist has been able to make twenty determinations of sulphur in six hours.

The determination of sulphur in coals and cokes, as described in this paper, is, in its essential features, a combination of parts of two methods already in use. These parts are, first, the process used by Sundstrom¹ for the complete oxidation of coals by means of sodium peroxide; second, the method of Andrews² for the volumetric estimation of the sulphur thus formed.

In carrying out these processes, however, various modifications have been introduced in order to accomplish, as perfectly as possible, the end in view; namely, the accurate, rapid, and convenient estimation of sulphur in coals and cokes. This object is satisfactorily accomplished by following the method as outlined below.

APPARATUS AND SOLUTIONS.

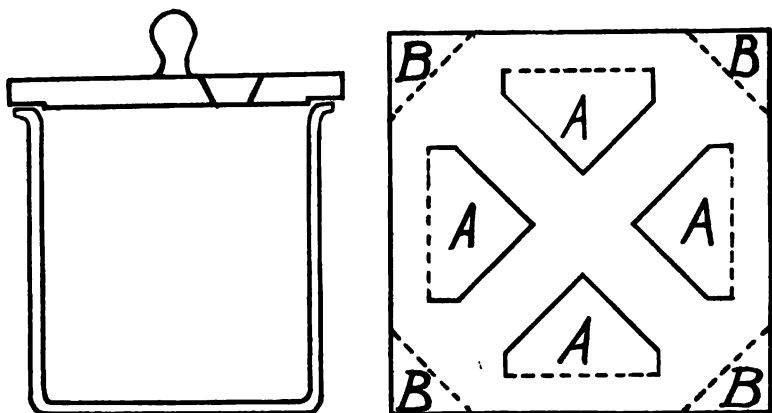
Crucible.—A soft steel crucible of about 40 cc. capacity, the lid being perforated with a small hole for the introduction of the igniting wire.

¹ This Journal, February, 1903.

² *Am. Chem. J.*, 11, 367; *J. Anal. Chem.*, 4, 73 (1890).

Crucible Stand.—Any arrangement suitable for holding the crucible firmly in place and out of contact with the beaker during the peroxide combustion.

The following diagrams show the form of crucible and stand used in this laboratory:



Crucible.

Thickness of walls and bottom of crucible, $\frac{1}{16}$ inch.
Hole in cover, diameter at top, $\frac{1}{4}$ inch.
Hole in cover, diameter at bottom, $\frac{3}{16}$ inch.
Other dimensions as shown in diagram.
The crucible and lid are nickel-plated.

Stand.

The stand is made from a sheet of aluminum, 2 inches by 2 inches, cutting as indicated by the heavy lines, then bending upward at right angles the four points marked "A," and downward at right angles the four points marked "B," making the bends along the dotted lines.

Barium Chromate Solution.—A solution of 23 grams pure barium chromate in a mixture of 80 cc. concentrated hydrochloric acid and 920 cc. water. With the use of commercial C. P. barium chromate, much trouble has been experienced because of its impurity. A suitably pure barium chromate may be prepared by adding a dilute potassium chromate solution to the theoretical quantity of barium chloride, also in dilute solution, and then washing the precipitate thoroughly.

Sodium Thiosulphate Solution (tenth-normal).—24.8 grams of the pure crystallized salt dissolved in water and the solution diluted to 1 liter.

Iodine Solution (tenth-normal).—12.69 grams iodine dissolved in a solution of 18 grams potassium iodide in 50 cc. water and the mixture diluted to 1 liter.

Starch Solution.

THE DETERMINATION.

Introduce into the crucible 16 grams sodium peroxide and 0.7 gram coal (or $11\frac{1}{2}$ grams sodium peroxide and 0.7 gram coke), and mix thoroughly by means of a small spatula. Cover, and place the crucible on its stand in a 20-ounce beaker of water, in such a way that the lower half only is immersed and the base of the crucible is slightly raised from the bottom of the beaker. Ignite the contents by thrusting a red-hot wire through the hole in the cover into the mixture. Complete fusion and combustion take place almost instantaneously. After three minutes or more, remove the stand and tip the crucible over on its side in the water. The fusion dissolves in a few moments and the crucible is then rinsed and removed. Add hydrochloric acid to the solution until distinctly acid, and boil. To the boiling liquid add ammonia until a few drops in excess, let boil vigorously a minute or two, then add 15 cc. of barium chromate solution and boil another minute. Add sufficient water to the boiling solution to make its volume 200 cc., then ammonia until several drops in excess, and continue boiling vigorously for one or two minutes longer. Allow to settle a few moments, filter and wash the precipitate twice thoroughly, using from 20 cc. to 30 cc. of hot water for each washing.

Add about 1 gram potassium iodide crystals to the filtrate, cool to 30°C ., add 5 cc. hydrochloric acid, then run in the thiosulphate solution until the end-point is reached. The presence of a few cubic centimeters of starch solution renders the end-point more distinct. Titrate back, if necessary, with the iodine solution.

$$\text{cc. N/10 Na}_2\text{S}_2\text{O}_3 \times 0.153 = \text{per cent. S.}$$

The determination depends, of course, on the fact that the precipitation of barium sulphate liberates an equivalent amount of chromic acid, which remains in solution as ammonium chromate when the excess of barium chromate is precipitated by ammonia.

REMARKS.

The directions for the peroxide combustion should be followed with especial care, for, if less sodium peroxide is used than the directions require, the reaction may be explosively violent; and, on the other hand, if too much sodium peroxide is used, the combustion will be incomplete. Also, the thorough mixing of the

fuel with the peroxide must not be neglected or an explosive and incomplete reaction will result.

After each addition of ammonia, the solution is boiled to remove most of the excess, but it should still remain slightly ammoniacal. The addition of the barium chromate does not always precipitate the sulphate immediately, but the subsequent boiling for one or two minutes insures complete precipitation. The final washing of the precipitates, if carried too far, will dissolve precipitated chromate and thus introduce an error. It has been found that two washings, using a small amount of hot water for each, produces the desired effect of thoroughly removing the chromate in solution without decomposing the precipitate.

RESULTS.

Up to the present time more than 1000 determinations by this method have been made in this laboratory. The accuracy of the results has been tested by comparison with the Sundstrom method, with the Eschka method, and by tests on solutions of known sulphate content. A number of the results thus obtained are cited below. The determinations on coal sample No. I were made independently by three analysts, each making two tests by the volumetric and two by the Eschka method. The four volumetric determinations of coke sample No. I required exactly one hour's time, showing the extreme rapidity as well as the accuracy of the method.

		Soft coal samples.				Coke samples.	
		I.	II.	III.	IV.	I.	II.
Per cent. S, volumetric method.		1.95					
		2.03				0.71	
		1.97	1.26	1.16	1.06	0.70	1.43
		1.98	1.26	1.16	1.06	0.70	1.41
		2.01	1.30		1.02	0.75	
		2.04					
Per cent. S, Eschka method.		2.03				0.75	
		2.06				0.68	
		2.04	1.30	1.20	1.05		
		2.06			1.07	0.70	
		2.04				0.70	
		2.00					
						Per cent. S, Sundstrom method.	1.47 1.42

Solutions, each containing 23 grams sodium chloride, a little iron, and a known quantity of sulphate (hence practically of the same composition as the solution obtained by the peroxide fusion of a coal) gave the following results:

Per cent. S present	0.46	0.914	1.37	2.29	0.98	1.96
		0.91			0.96	
Per cent. S found.....	0.45	0.90	1.35	{ 2.33	{ 1.02	1.93
		0.92		{ 2.36	{ 0.99	
					0.99	

CONCLUSION.

The results of all tests show that the method carried out in accordance with the above directions, is accurate to within a few hundredths of a per cent., and is so rapid that an average of two or even three complete determinations per hour can be accomplished. It can be used with especial advantage where large numbers of sulphur determinations are required, since in such a case its saving in time and in the use of platinum becomes an important item.

The method can be successfully employed not only for the determination of sulphur in coals, but also, with suitable modifications, for the determination of small percentages of sulphur in a large number of organic and inorganic substances.

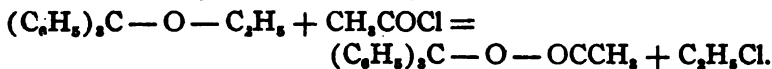
LABORATORY OF THE SOLVAY PROCESS CO.,
SYRACUSE, N. Y.

ON TRIPHENYLMETHYL ACETATE.

BY M. GOMBERG AND G. T. DAVIS.

Received October 22, 1903.

HEMILIAN,¹ the discoverer of triphenylcarbinol, observed that the carbinol reacts with acetyl chloride, giving rise to hydrochloric acid and a crystalline mass which, on exposure to moist air, loses acetic acid and changes back to the carbinol. With acetic anhydride and with benzoyl chloride he obtained unstable esters, which were readily decomposed by water and by alcohol. Later, Allen and Kölliker² described a method for the preparation of triphenylmethyl acetate, which consisted in the action of acetyl chloride upon triphenylcarbinol ethyl ether,

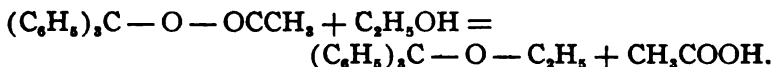


They claim to have identified the escaping gas as ethyl chloride, and give the melting-point and the solubilities, as well as the

¹ *Ber. d. chem. Ges.*, 7, 1207 (1874).

² *Ann. Chem. (Liebig)*, 227, 116 (1885).

analysis, of the acetate. Recently, Herzig and Wengraf,¹ in connection with their studies on the acetyl derivatives of aurin, rosolic acid and benzaurin, repeated the experiments described by Hemilian, and by Allen and Kölliker in regard to the acetyl compound. Herzig and Wengraf find that the acetyl derivative, as obtained by them, possesses greater stability than ascribed to it by Hemilian. They also claim that the original method of Hemilian, the action of acetyl chloride directly upon the carbinol, is to be preferred to the method of Allen and Kölliker, who employed the triphenylcarbinol ethyl ether instead of the carbinol itself. Hemilian, as well as Herzig and Wengraf, concluded that the product described by them was the acetyl derivative, because, on treatment with water, the carbinol was regenerated, apparently by saponification. With alcohol, the acetyl compound gave the triphenylcarbinol ethyl ether, the reaction being the reverse of that which gave Allen and Kölliker the acetyl derivative,



It is on the basis of the above-mentioned researches that the statements in the literature² in regard to triphenylmethyl acetate are made. In the following pages it will be shown that the reactions described by the different investigators lead, not to the formation of the acetyl derivative but simply to that of triphenylchlormethane; that the acetyl compound, prepared by us by an indirect method, possesses properties different from those assigned to it by others, and that the acetyl compound could not exist under the conditions of the experiments which were used for its preparation.

Action of Acetyl Chloride.—One of us reported³ that by treating triphenylcarbinol ethyl ether with acetyl chloride pure triphenylchlormethane was obtained. The discrepancy between these results and those of Allen and Kölliker, who claimed to have obtained, by this reaction, triphenylmethyl acetate, necessitated a careful revision of the experiments.

¹ *Monatsh. Chem.*, **22**, 612 (1901).

² "Beilstein," II, 1083; V. Meyer u. P. Jacobson, "Lehrbuch," II, 2, 109; "Richter," 3rd Ed., 353; Remsen's "Organic Chemistry," 355; Baeyer u. Villiger: *Ber. d. chem. Ges.*, **38**, 3015, etc.

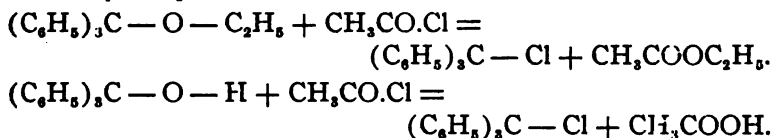
³ This Journal, **24**, 618 (1902).

(1) The ethoxy compound, $(C_6H_5)_3C-OC_2H_5$, was made by boiling triphenylchlormethane with absolute alcohol. The product was recrystallized once from alcohol and twice from petroleum ether. The substance was thus obtained in pure white crystals, melting sharply at $83^\circ C$. To 2 grams of this ethoxy compound was added an amount of freshly distilled acetyl chloride just sufficient for solution, and the mixture was boiled for about an hour. Upon cooling slowly, large white crystals, 1.5 grams, separated. After recrystallization, the product gave a melting-point of $112^\circ C$., and was identified by its properties and by analysis as pure triphenylchlormethane.

(2) Two grams of the ethoxy compound were dissolved in cold acetyl chloride. A small amount of heat was generated by the reaction, and crystallization commenced at once. A little petroleum ether was added and the mixture cooled in ice. The crystals, 1.8 grams, were washed with petroleum ether, recrystallized and analyzed. They melted at $111^\circ C$., and consisted of pure triphenylchlormethane. An analysis gave 12.91 per cent. chlorine; calculated, 12.75 per cent.

(3) The triphenylcarbinol, instead of the ethoxy compound, was next tried. Two grams were dissolved in acetyl chloride. The solution was of a violet color and changed to a dark red as the reaction progressed. Some heat was evolved in this reaction also. The crystals which separated on cooling, 1.7 grams, showed, on recrystallization, a melting-point of $109^\circ C$., and were found to consist of pure triphenylchlormethane. The analysis gave 12.67 per cent. chlorine.

The action of acetyl chloride upon triphenylcarbinol and upon its ethoxy compound is, therefore, as follows:



Action of Acetic Anhydride.—(1) One gram of the pure carbinol was boiled for an hour with pure acetic anhydride. The acid was then distilled off under diminished pressure and the residue recrystallized from petroleum ether. The product, 0.9 gram, melted at $160^\circ C$., and was found to consist of unchanged carbinol.

(2) Another sample of triphenylcarbinol was boiled with acetic anhydride and anhydrous sodium acetate. The solution was filtered hot and concentrated, as before, under diminished pressure. The resulting product, which melted at 159°C ., was again unchanged carbinol.

Herzig and Wengraf obtained, on boiling the reaction product from acetic anhydride and the carbinol with alcohol, triphenylcarbinol ethyl ether. But, as they themselves observe, this cannot be taken as a conclusive proof that the acetyl compound was the cause of its formation, because the carbinol itself gives, on boiling with alcohol in presence of a small amount of acetic acid, the ethyl ether compound. The experiments described above show that in reality no acetyl compound was formed.¹

Triphenylmethyl Acetate.—We next prepared the acetyl compound by an indirect method,—by the action of silver acetate upon triphenylchlormethane. Four grams of triphenylchlormethane were dissolved in benzene, mixed with an excess of silver acetate and boiled, with reflux condenser, for two hours, moisture being carefully excluded. The solution was filtered hot and the excess of benzene distilled off. The crystals, which separated out on cooling with ice, were washed with petroleum ether and then recrystallized, twice from petroleum ether and twice from acetic ether. The melting-point of the crystals remained constant at $87^{\circ}\text{--}88^{\circ}\text{C}$. The analysis gave:

	Calculated for (C_6H_5) ₃ CO ₂ CCH ₃	Found.	
		I.	II.
Carbon.....	83.44	82.98	83.37
Hydrogen.....	6.01	6.06	5.99

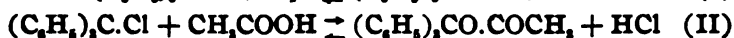
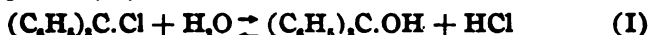
The acetyl group was determined in the usual manner, by boiling the substance with an alcoholic solution of potassium hydroxide and titrating the excess of the alkali with a standard solution of acid. Calculated for (C_6H_5)₃CO.OCCH₃, acetyl, 15.25 per cent.; found, 13.19 and 13.07 per cent.

We have also prepared the acetyl compound without the employment of heat. One sample of triphenylchlormethane was suspended in absolute ether, an excess of silver acetate added, and the whole shaken for three weeks at the temperature of 25°C . A second sample, dissolved in benzene, was treated in the same way. In both instances, almost quantitative yields of very pure

¹ Compare Bistrzycki und Herbst: *Ber. d. chem. Ges.*, 35, 3133 (1902).

triphenylmethyl acetate were obtained. The acetyl compound melts, as stated, at 87°-88° C. It is very soluble in the usual organic solvents, and, like so many other triphenylmethyl derivatives, shows a tendency to separate from concentrated solutions in the form of an oil, which, on scratching, changes to a crystalline mass. Acetic ether gives the best appearing crystals. The compound is readily decomposed by water and by alcohol.

Action of Acetic Acid upon the Acetyl Compound.—It was found by one of us¹ that triphenylchlormethane reacts but slowly with cold glacial acetic acid, but quite appreciably when the solution is heated. It was also found² that hydrochloric acid acts upon triphenylcarbinol in acetic acid even when the latter contains as much as 10 per cent. water, and gives triphenylchlormethane. It was suggested that while in a 90 per cent. acetic acid solution the reaction is a reversible one in regard to carbinol (I), in absence of water it is similarly so in regard to the acetyl compound (II).



Experiment, however, shows that this is not the case in (II). Two grams of triphenylchlormethane were heated with a large excess of carefully purified glacial acetic acid on the water-bath, and a constant stream of dry carbon dioxide was passed through the solution for twenty hours. A careful examination of the residue, obtained on removing the acetic acid under diminished pressure, showed that, in addition to some triphenylchlormethane, it contained triphenylcarbinol, but none of the acetyl compound.

Action of Acetyl Chloride upon the Acetyl Compound.—The acetyl chloride for this experiment was carefully fractionated. A stream of thoroughly dried carbon dioxide was then passed through the chloride in order to free it completely from any hydrochloric acid gas which it might have contained in solution. One-half gram of pure triphenylmethyl acetate was gently warmed with the acetyl chloride. The excess of the liquid was removed in a stream of dry air, and the crystalline residue was dried in a vacuum dessicator over soda-lime. It melted at 109° C., and proved to be pure triphenylchlormethane. The analysis gave 12.97 per cent. chlorine; calculated, 12.75 per cent.

¹ *Ber. d. chem. Ges.*, 26, 379 (1903).

² *Ibid.*, 26, 384 (1903).

As Hemilian, Allen and Kölliker, and Herzig and Wengraf have all used acetyl chloride in the preparation of the substance described by them as triphenylmethyl acetate, and as the latter is decomposed by that reagent, it follows that the substance described by them as triphenylmethyl acetate, and as the latter it was, we believe, triphenylchloromethane. The latter would give, on treatment with water or with alcohol, the same products as the acetyl compound: the carbinol or the ethoxy compound. In fact, this is true of all the salts of triphenylmethyl: the halides, the sulphate, the picrate, etc., are readily hydrolyzed.

ANN ARBOR, MICH.,
September, 1903.

ON THE POSSIBLE EXISTENCE OF A CLASS OF BODIES ANALOGOUS TO TRIPHENYLMETHYL.

[PRELIMINARY NOTICE.]

BY M. GOMBERG.

Received October 12, 1903.

IN THE several papers which I have published on the subject of triphenylmethyl, some important features in regard to the behavior of that substance were brought out.

(1) The extreme unsaturation of the compound, as evidenced by the action of atmospheric oxygen and of iodine upon it.

(2) The unusual property possessed by that unsaturated hydrocarbon of entering into combination with different oxygen compounds, such as ethers, esters, etc. It appeared probable that these combinations represent compounds wherein the oxygen acts as being tetravalent. It might be added here that triphenylmethyl unites with equal readiness with nitriles.

(3) Triphenylmethyl may be considered as a distinctly basic radical. This furnishes an explanation why triphenylchloromethane, also the bromide and the iodide, are *salts*, as judged by their purely chemical behavior, as well as by the physico-chemical tests; these halides, dissolved in liquid sulphur dioxide, are true electrolytes.¹ The same is true of the sulphate, as was found by Mr. L. H. Cone² in this laboratory. Even triphenyl-

¹ Gomberg: *Ber. d. chem. Ges.*, **35**, 2403 (1902); Walden: *Ibid.*, **35**, 2018 (1902).

² Mr. L. H. Cone, holder of a research assistantship to the Carnegie Institution, will publish his results in full later.

methyl itself possesses. in that solvent, a decided electrical conductivity, as has been recently shown by Walden.¹

(4) Under the influence of catalyzing agents, such as dilute hydrochloric acid in benzene, ether, or some other solvent, triphenylmethyl is readily condensed to hexaphenylethane.²

It could hardly be expected that, whatever the constitution of triphenylmethyl, there should not be some other similar compounds capable of existence. The reaction which served for the preparation of triphenylmethyl was accordingly further studied, and an attempt has been made to apply it to compounds analogous to triphenylchlormethane. The following substances were subjected to this test:

Para-ditolylphenylchlormethane, $(\text{CH}_3\text{C}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{C.Cl}$.

Tritolylchlormethane, $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{C.Cl}$.

Paratrinetrotriphenylchlormethane, $(\text{NO}_2\text{C}_6\text{H}_4)_3\text{C.Cl}$.

Paratrimethoxytriphenylchlormethane, $(\text{CH}_3\text{O.C}_6\text{H}_4)_3\text{C.Cl}$.

In every case the initial stage of the reaction has been found to be the same as when triphenylchlormethane itself had been employed. A solution of the latter in benzene or in ether, when treated with zinc, silver, or mercury, assumes instantly a yellow color, which, as has been conclusively shown, is due to the formation of triphenylmethyl. Now, when any one of the four above-mentioned derivatives of triphenylchlormethane is treated in the same manner, the reaction is strikingly similar to the one with triphenylchlormethane itself. The introduction of the metal into a solution of those substances is followed in every case by the instantaneous formation of a substance which imparts color to the solution. Moreover, just as the exposure to air in the case of triphenylmethyl brings about rapid oxidation of the hydrocarbon and the consequent decolorization of the yellow solution, so also in the case of the other four instances; exposure of the solutions to air destroys their color at once—due, no doubt, also to oxidation.

But while in the case of triphenylmethyl the oxidation is comparatively simple, and the resulting product, the peroxide, can be readily isolated, the oxidation by the atmospheric oxygen in the other instances is more complex. So far, I have succeeded in isolating the oxidation product pure enough for analysis only in one

¹ *Ztschr. phys. Chem.*, **43**, 443 (1903).

² *Ber. d. Chem. Ges.*, **35**, 3914 (1902); **36**, 376 (1903).

other instance, namely, in the case of the unsaturated hydrocarbon from tritolychlormethane. Indeed, although there can be but little doubt that the action of metals upon the different triphenylchlor-methane derivatives is probably the same in all instances, yet, in my experience, each case requires, for the successful course of the reaction, different experimental conditions. The nature of the metal, as well as the nature of the solvent, is of considerable influence upon the progress of the reaction. The subject becomes more difficult still because some of the chlor-compounds, as, for instance, the trinitrotriphenylchlormethane, are only slightly soluble in the usual organic solvents, which necessitates the use of large volumes of liquids.

The halides of triphenylchlormethane—the chloride, bromide, and iodide—are colorless in the solid state and also when dissolved in solvents which possess no ionizing power. But when dissolved in liquid sulphur dioxide, which does possess this power to a large extent, these halides dissociate into ions, $(C_6H_5)_3C^+$ and Cl^- , as was proved by the electrical conductivity of the solutions. Moreover, such dissociation is invariably accompanied by the formation of a yellow color in the solvent. It was suggested¹ that the color was due to the ion $(C_6H_5)_3C^+$. Since the free hydrocarbon, triphenylmethyl itself, while colorless in the solid state, on dissolving gives yellow solutions, it was inferred that the hydrocarbon exists in solution as ions $(C_6H_5)_3C^+$ and $(C_6H_5)_3C^-$. The fact that triphenylmethyl, dissolved in liquid sulphur dioxide, shows very considerable electrical conductivity, argues, it seems to me, in favor of this view. There remains yet to account for the relation which exists between the two states of triphenylmethyl, the colorless solid and the yellow when in solution. If, however, it be true that the color of the solution of triphenylmethyl is really due to the latter existing in solution in the ionic state, then it must follow that a variation in complexity of the radical should also cause a variation in the color of the radical when the latter is in solution and hence in the ionic state. This is actually the case. Solutions of triphenylchlormethane acquire, on the addition of metals, a distinctly yellow color. The ditolylphenyl- and especially the tritolychlormethane, when subjected to the similar treatment, give orange solutions with quite a perceptible tinge of red. Trinitro-

¹ Gomberg: *Ber. d. chem. Ges.*, 35, 2406 (1902).

triphenylchlormethane, even in minute quantities, gives, on the addition of metals (silver), a beautiful greenish-blue solution which changes, on warming, first to a violet-red and finally to a genuine fuchsine-red. On cooling, the blue color is restored; on exposure to air the solution is at once decolorized.

I shall continue the study of this reaction and shall extend it to other derivatives of triphenylhalogenmethane.

ANN ARBOR, MICH.,
September, 1903.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

AN EFFICIENT ASBESTOS OR GRAPHITE MUFFLE.

BY J. M. PICKEL AND C. B. WILLIAMS.

Received October 15, 1903.

AT THAT point in the determination of potash in fertilizers, where ammonium salts and the excess of sulphuric acid are driven off, it was formerly the practice in this laboratory to accomplish the volatilization by placing the platinum dish on the top of the glass chimney of an Argand gas-burner, such as is commonly used for illuminating purposes. To afford air-vent and gas escape, the dish rested on small wires (of iron) bent over the edge of the chimney. A battery of ten or twelve of these burners was aligned on the same gas-pipe.

After excess of acid was evaporated and the ammonium salts more or less volatilized, the dishes were removed from the Argand burners to the blast-lamp, and there, at a red heat, the volatilization completed and the organic matter destroyed. In hope of obviating the necessity of transferring the dishes to the blast, one of us (Pickel) introduced, during the winter of 1900, the following modification:

The chimneys were cut down to a length of about 4 cm., and the dishes brought into close proximity with the flame. The dishes were, moreover, enclosed in asbestos cups, in the bottom of which were cut round holes of such diameter as to fit snugly over the chimneys which were thus made to support the cups. An asbestos lid, having a vent hole of about 2 cm. diameter, covers each cup. Each platinum dish rested on a pipe-stem triangle, or

other suitable support placed on the bottom of the cup. It was found that the dish, thus muffled, could, after excess of acid had been driven off by a low flame, be easily brought to a red heat by merely turning up the flame; all ammonium salts could be volatilized completely, and organic matter destroyed, thereby obviating the use of a blast-lamp, except in rare cases. As the intense heat generated in the muffle softened, and, after a few days, distorted the glass support, it was, therefore, dispensed with, and a small asbestos cylinder, having in its side a narrow slot, or small, round hole through which to see and regulate the flame, substituted.

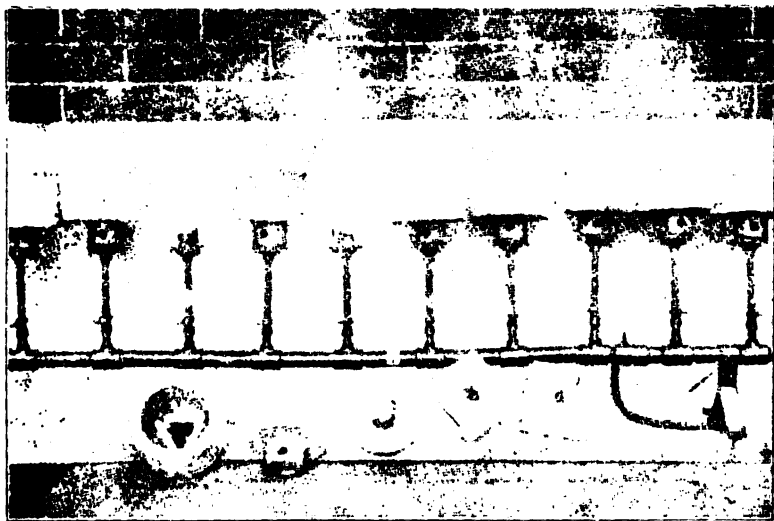
The material used in making this little muffle was asbestos board of about 0.6 cm. thickness. After cutting the board to proper shape and size, it was saturated with water, and, while wet, formed into a cylinder by rolling it around a tin can, or bottle, or other suitable core, and left till dry. The bottom was then fitted in and the whole held securely together by wires bound around near the top and bottom.

A battery of twelve of these little muffles was used throughout the greater part (two or three months) of a fertilizer season, and 500 or 600 potash determinations made with them. All incinerations of cotton-seed meal, cotton-seed hulls and tobacco stems were made in them, the usual larger and cumbersome muffles for that purpose being entirely dispensed with. Slightly changed in form, the muffles are, of course, equally suitable for use with a Bunsen burner. They were thus found efficient for roasting small assays of sulphurous gold ores, the finely powdered ore being contained in an ordinary evaporating dish.

Although the idea of these muffles—a separate muffle for each dish or crucible—grew out of the desire to facilitate the work of volatilization and incineration, it is not new. (The Erdmann furnace, which is figured and described in the chemical catalogues as a clay cylinder on a tripod over a Bunsen burner, involves the same idea.)

The efficiency and convenience of these little muffles for incinerations, ash determinations, roastings and volatilizations, and the ease with which any one can make them for himself, should create for them a place in the laboratory. But for daily use, year in and year out, they are not sufficiently durable when made

of asbestos, as above described. One of us (Williams) sought to remedy this defect, first, by constructing the muffles of metal (copper) and covering them inside and out with asbestos. But these, although in other respects satisfactory, were lacking in durability; the metal oxidized rapidly, and the asbestos needed renewal every few months. The material finally adopted (by him) was graphite, with a jacket of asbestos on the outside. This has proved altogether satisfactory. A battery of twelve of these graphite muffles, aligned on the same gas-supply pipe, and each heated by an Argand gas-burner, has now been in daily use for about two years in our laboratory, and has entirely superseded the usual form of muffle, for incinerations, ash determinations and the like. A point of special convenience with this piece of apparatus is that one or more, up to a dozen determinations may be made at one time, and that each is under separate control and regulation. The lids in use consist of an asbestos board, a plate of aluminum and a sheet of platinum riveted together; the asbestos forms the top of the lid and the platinum



the bottom, its object being cleanliness. But less-costly graphite covers answer quite as well. In the center of each lid is a vent-hole of about 3 cm. diameter. The muffles may be of any size. Ours have the following dimensions: The main body or re-

ceptacle, diameter (internal) and depth (internal), each 9.5 cm.; thickness of wall, 1 cm.; the small cylinder support, length, 3.5 cm.; diameter (adjusted to the size of burner in which it is to rest), in our case, 5.2 cm. outside, and 3.5 cm. inside.

These muffles may, of course, be used with any common Bunsen burner by placing them on a tripod.

The accompanying cut shows the parts of the battery of muffles:

1 is the gas-supply pipe, 2.5 cm. in diameter; 4 is a smaller pipe, provided with an air-hole and gas-cock, which feeds the Argand burner above; 2 shows the muffle in position and without asbestos covering; at 3 is a small hole through which the gas is lighted, and through which the flame may be seen and regulated; 5 gives an inside view of the muffle; 6 shows the under part of a muffle; 7 shows the top side of a graphite lid, the central vent-hole of which is hidden by its handle; and 8 and 9 are top and bottom views of the asbestos-aluminum-platinum lids.

REVIEW.

RECENT WORK IN INORGANIC CHEMISTRY.

BY JAS. LEWIS HOWE.

Few notable papers have appeared during the past year on theoretical inorganic chemistry. Perhaps the most important is one by Abegg¹ on a new theory of valence. The author assumes the existence of two kinds of valence, with opposite polarity, in each atom. These he calls normal valence and contra-valence. The sum of the valences of an atom is eight. Thus chlorine has a negative normal valence of one and a positive contra-valence of seven. Negative contra-valences are much weaker than positive, since positive electrons are much more firmly attached to matter than the negative. The inert gases have a normal valence of zero and an (unexercised) contra-valence of eight. In his paper, Abegg applies these conceptions to the so-called molecular compounds.

In two papers,² Werner has developed his theory of primary and secondary valences with reference to the constitution of the ammonium and the oxonium compounds. Locke³ has again attacked the theory of electro-affinity of Abegg and Bodländer, and holds that while the electro-affinity of the elements bears a close and interesting relation to the properties of many salts, it does not furnish a rational principle for chemical classification.

Erdmann claims⁴ that the distinction enunciated by him in

¹ *Vid. Skrift.* I, 1902, No. 12.

² *Ann. Chem. (Liebig)*, 322, 261, 296.

³ *Am. Chem. J.*, 28, 403.

⁴ *Ztschr. anorg. Chem.*, 32, 404.

1892, between metals and non-metals, *viz.*, that metals are those elements whose molecules consist of single atoms, while non-metals are those whose molecules contain several atoms, has been confirmed by all the more recent work along this line. On the other hand, Martin,¹ reasoning from the fact that in the same group the metallic characteristics of an element increase with the atomic weight and that among the non-metals the metallic character increases with the temperature, draws the conclusion that the metallic and non-metallic conditions are merely phases which each element can assume. At higher temperatures non-metals become metallic, their electrical conductivity increasing rapidly; in the vicinity of absolute zero, metals become non-conducting metalloids.

In the consideration of the periodic table, Brauner² suggests that the difficulty of accounting for the place of the rare earths will be minimized if we put them as a group in the place usually assigned to cerium. Thus, in this place we shall have *Ce, etc., 140-178*, followed immediately in the next space by *Ta 184*. In this way the vacant ninth period of Mendeléeff's table disappears. Brauner begins his table with Group 0, which is made up of the inert gases.

The study of double salts continues to attract increasing attention, though no satisfactory theory of their constitution has yet appeared. An important contribution to the chemistry of the double halides is the *Habilitationsschrift* of P. Pfeiffer.³ Following up the systematic treatment of the double chlorides by Werner, he takes up the bromides and iodides from the same standpoint, and after a theoretical discussion of these salts, he gives a systematic survey of the whole field, with references to the literature. In connection with his study of vanadium salts, in which many new double halide compounds have been prepared, Ephraim⁴ discusses these salts from a theoretical standpoint, holding that their constitution is largely dependent upon the atomic volume of the constituent elements. In particular, he formulates the law that the number of halogen alkali molecules which can unite to the halide of the heavy metal acting as a central nucleus, decreases with the increasing atomic weight of the positive metal. Grossmann⁵ denies that the facts accord with this law. In a number of cases, such as $\text{PbBr}_2 \cdot 4\text{CsBr}$, the highest value is reached with the cesium salt. Rubidium and ammonium salts often show a strong analogy which may be conditioned by the fact that they possess a similar atomic volume. Nor do the double cyanides, which are, according to Werner, of the same character as the halides, follow Ephraim's law. Grossmann's conclusion is that

¹ *Chem. News*, 86, 295.

² *Ztschr. anorg. Chem.*, 32, 1.

³ Partially republished in *Ztschr. anorg. Chem.*, 31, 191.

⁴ *Ber. d. chem. Ges.*, 36, 1177.

⁵ *Ibid.*, 36, 1600.

no comprehensive rule can be, at present, laid down regarding the composition of double salts. The discussion is being continued by Ephraim,¹ who has also prepared a series of new antimony double salts, and by Grossmann,² while Pfeiffer³ and Jordis⁴ both fail to find an experimental foundation for Ephraim's law. The probability is that there is a considerable sub-stratum of truth in the so-called law, but that it represents only a part of the truth. At all events, it is encouraging to find an increasing number of keen minds attacking this important problem of the double salts. Mention should be made, in this connection, of the interesting class of triple thiocyanates under investigation by Wells,⁵ and the double periodates and manganese studied in the same laboratory by Price.⁶

In an address before the Fifth International Congress of Applied Chemistry at Berlin, Moissan gave a review of his work on the metallic hydrides. The alkali and alkali-earth hydrides are definite crystalline compounds and have nothing of the nature of hydrogen alloys. They are strong reducing agents, decomposing water with the evolution of hydrogen, forming formates with carbon dioxide and hydrosulphites with sulphur dioxide. With acetylene they form double compounds, of which K_2C_2, H_2C_2 is a type; on heating the latter, acetylene is evolved and the metallic carbide left.

A new preparation of nitrides has been discovered by Guntz.⁷ When lithium nitride acts upon metallic chlorides, much heat is evolved and the corresponding nitride formed. This appears to be a method of general application. Lithium hydride seems to give a similar reaction, but it is so violent that it has not yet been possible to isolate the hydride, which is formed.

Moissan continues to enlarge our knowledge of the silicides. While it has been found very difficult to prepare the potassium and sodium silicides corresponding to silicon-ethane, Si_2H_6 , the lithium compound, Li_6Si_2 , is prepared by direct union of the elements in a vacuum. It is naturally a very active substance, decomposing water and acids generally with evolution of hydrogen, but when very concentrated hydrochloric acid is used the silicon-ethane is obtained, which is collected as a liquid by the use of liquid air.⁸ Moissan has also prepared two silicides of vanadium, V_2Si and VSi_2 . Lebeau has studied the silicides of cobalt, manganese and chromium. In the case of the last two metals, he has investigated, from a physical standpoint, the equi-

¹ *Ber. d. chem. Ges.*, 36, 1815, 1912.

² *Ibid.*, 36, 2499.

³ *Ibid.*, 36, 2519.

⁴ *Ibid.*, 36, 2539.

⁵ *Am. Chem. J.*, 28, 245; 29, 474; 30, 184.

⁶ *Ibid.*, 30, 182.

⁷ *Compt. Rend.*, 135, 738.

⁸ *Ibid.*, 134, 1083, 1549; 135, 1284.

librium which exists between copper, silicon and manganese, and copper, silicon and chromium. This has enabled him to prepare several new silicides.¹

Muthmann and Kraft² have prepared the hydrides and nitrides of cerium and lanthanum by burning the metals in hydrogen or nitrogen. In hydrogen, cerium ignites at 250° , while in pure oxygen its kindling temperature is little above 150° . In nitrogen, cerium does not ignite until 850° is reached. The kindling temperature of lanthanum is, in each case, somewhat higher than that of cerium. The hydrides and nitrides of these metals are stable in dry air, but are quickly decomposed by water or in the presence of moisture.

Several articles have appeared from the laboratory at Odessa, continuing the work of Pissarjewski on the compounds of inorganic salts and acids with hydrogen peroxide. The carbonates, arsenates, tungstates, uranates, vanadates, and the rare earths are included in this list. There is a very decided question as to whether many of these compounds are to be considered as true peroxides, or whether some of them, which have been designated as pseudo-peroxides, should not rather be considered as compounds in which the hydrogen peroxide is present in the form of a so-called peroxide of crystallization. This is discussed by Tanatar in a recent paper,³ and by Willstätter.⁴ A new class of peruranates has also been described by Alloy,⁵ having the formula M_2UO_6 . In a lecture at the meeting of the Verein of the German chemists at Düsseldorf, Staedel illustrated the preparation of pure hydrogen peroxide. A 95 per cent. solution was solidified by the ether-carbon dioxide mixture. When, to a new portion of the 95 per cent. solution, at a temperature of -10° , a little of the solid is added, crystals of pure hydrogen peroxide begin to form. On recrystallization, these consist of 100 per cent. hydrogen peroxide, and this is suggested as the safest method of preparing the anhydrous compound. The crystals are fairly stable, but are exploded at once by contact with platinum black or pyrolusite. With the monohydrate of sulphuric acid, ozone is at once formed. Some interesting notes on ozone are contributed to the *Berichte* (35, 2902) by Arnold and Mentzel. Tetramethyl-*p-p'*-diaminodiphenylmethane (tetra-base for short) is proposed as the best reagent for gaseous ozone, to differentiate it in the presence of other gases which have action upon starch-iodide paper. Ursol D, which had been suggested by Chlopin for a similar purpose, is shown to be useless, as its supposed characteristic reaction is caused by the impurities present and not by ozone.

¹ *Compt. Rend.*, 136, 231, 1329.

² *Ann. Chem. (Liebig)*, 325, 261.

³ *Ber. d. chem. Ges.*, 26, 1893.

⁴ *Ibid.*, 26, 1828.

⁵ *Bull. Soc. Chim.* (3), 29, 292.

Dudley¹ has studied the action of sodium peroxide on several more metals. With nickel, $\text{Ni}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is formed, which loses water at 240° . It is unlike Daubigny's Ni_2O_4 in its properties. Iron gives $\text{Fe}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in tabular, magnetic crystals. Gold is rapidly attacked, but the oxide formed is immediately decomposed, giving spongy gold. Silver is also rapidly acted upon with the formation of gray crystals, which seem to be a lower oxide. Spongy platinum burns with the peroxide like tinder, giving after washing, $\text{Pt}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$. On heating, the sesquioxide is left, which is a new oxide of platinum.

Moissan has continued his studies on fluorine, examining, in conjunction with Dewar, the action of the element at low temperatures.² The melting-point of solid fluorine was found to be -223° . The solid fluorine reacted with liquid hydrogen at -252.5° (20.5° absolute) with explosive violence. At -187° , the reactions of various compounds and elements with liquid fluorine are hardly less violent than at higher temperatures, its affinity being little in abeyance even at this low temperature. Iodine pentafluoride has been prepared by Moissan³ and proves to be so stable that it can be distilled in hydrogen without decomposition.

Starting from the fact that chlorine is liberated from hydrochloric acid by Caro's reagent, Wedekind⁴ has attempted the use of the analogous reaction for the preparation of fluorine. Caro's reagent, however, had no action upon hydrofluoric acid, neither fluorine being evolved directly, nor any trace of ozone, which might indicate that it had been temporarily formed.

By using a modification of the Goldschmidt process, the magnesium, aluminum, and oxides being taken in such proportions as to give the composition of the natural matrix of the diamond, von Hasslinger⁵ has succeeded in converting finely divided graphite into clear, octahedral diamonds of 0.5 mm. diameter. The interesting point about this synthesis is that the diamonds are formed by slow cooling in the absence of any considerable pressure.

A new variety of phosphorus has been prepared by Schenck,⁶ by heating white phosphorus to boiling in PBr_3 for ten hours. It is light red, resembling, in appearance, the ordinary red modification, and, like it, being physiologically inert, but, on the other hand, it is very active chemically, often more so than white phosphorus.

For the preparation of phosphine, Bodroux⁷ uses a crude aluminum or magnesium phosphide, made by igniting a mixture

¹ *Am. Chem. J.*, **28**, 59.

² *Compt. Rend.*, **136**, 641, 785.

³ *Ibid.*, **138**, 563.

⁴ *Ber. d. chem. Ges.*, **38**, 2267.

⁵ *Monatsh. Chem.*, **23**, 817.

⁶ *Ber. d. chem. Ges.*, **30**, 99.

⁷ *Bull. Soc. Chim.* (3), **27**, 568.

of 2 parts aluminum (or magnesium) and 1 part red phosphorus. The resulting mass gives off pure phosphine slowly on treatment with cold water, and more rapidly when the water is warm. Above 50° the phosphine is contaminated with hydrogen, as is the case when acids are used.

Stock and Hoffmann,¹ by the action of ammonia on phosphorus pentasulphide, have prepared a series of amino- and imino-thiophosphoric acids, and by the successive elimination of ammonia and hydrogen sulphide obtain at last phosphorus nitride, P_3N_3 . This interesting compound proves to be a white, insoluble, odorless and tasteless body, stable up to a low red heat. Although outside of the strict range of inorganic chemistry, it should be noted here that Michaelis and his pupils have developed much further the organic compounds containing both phosphorus and nitrogen, forming several hundred compounds.²

The metaphosphates have been subjected to a somewhat extended investigation by Warschauer,³ who finds that Fleitmann's dimetaphosphate is in reality a tetrametaphosphate. This result is confirmed both by the Ostwald-Walden valence law, and by the transference number of the sodium salt. When lead oxide is heated with phosphoric acid, if the temperature is kept below 400° , the tetrametaphosphate is formed, while above that temperature a different modification, Fleitmann's 'tetrametaphosphate,' appears, which is, in all probability, the hexametaphosphate. He also finds that the solutions of the hexametaphosphate decompose directly into the orthophosphate, but a small amount of the pyrophosphate is formed at the same time.

Erdmann and Unruh⁴ have made a study of the yellow modification of arsenic, first described by Linck in 1899. It is prepared by the rapid cooling of arsenic vapor, and must be immediately dissolved in carbon bisulphide or benzene to prevent its almost instant conversion into the ordinary metallic arsenic. Erdmann prepared a large quantity by collecting the vapor directly in carbon bisulphide. It may be obtained in solid form by cooling a saturated solution to -70° , but is exceedingly unstable. By the gradual action of light on the solution, a new red-brown modification of arsenic is obtained. The molecular weight of the yellow modification corresponds to the molecule As_4 . From the fact that vitreous arsenious oxide is formed by rapid cooling, Erdmann concludes that it contains a ring of four arsenic atoms, and he has succeeded in obtaining a small quantity of yellow arsenic by the reduction of this form of the oxide.

¹ *Ber. d. Chem. Ges.*, 36, 314.

² *Ann. Chem. (Liebig)*, 326, 129, 171, 220.

³ *Ztschr. anorg. Chem.*, 36, 137.

⁴ *Ibid.*, 32, 437.

The pentachloride of arsenic has been obtained by Baskerville and Bennett¹ by the action of chlorine on the trichloride at very low temperatures.

Our knowledge of the halide double salts of quinquivalent antimony has been very materially enlarged by Weinland and Feige,² who have prepared a series of double chloro- and bromo-antimonates. Most of these are derived from metachloro-antimonic acid, HSbCl_6 , and the corresponding bromo-acid. A second salt of quadrivalent antimony, Rb_2SbBr_6 , was also found.

After a study of sundry alloys of antimony, Stock and Dohrt³ find that the alloy of antimony with 2 parts magnesium is best suited for the preparation of stibine. This alloy is treated with hydrochloric acid, the gas is carefully dried and condensed by the use of liquid air. The fusing-point of stibine is -88° , its boiling-point -17° . When pure, it is fairly stable for a few hours, but is immediately decomposed at 150° .

By an examination of the composition of the vapor of a mixture of S_2Cl_2 and chlorine, Ruff⁴ finds that the supposed compound SCl_2 has no existence. The same is true of SBr_2 and SBr_4 ,⁵ while Boulouch⁶ has, by the use of the dilatometer, proved that none of the supposed compounds of sulphur and iodine have any claim to recognition. Russel and Smith⁷ have failed to find any evidence for the existence of Deninger's carbon monosulphide, but Thomsen later shows that it is really formed by the action of hot copper upon a mixture of carbon bisulphide and nitrogen, but it has not proved possible to isolate it.⁸

Contrary to the views of Ringer and Muthmann, that the supposed compounds of sulphur and selenium are isomorphous mixtures of the elements, Rathke⁹ considers that in this mixture there are present not less than two distinct compounds of sulphur and selenium. He suggests that it is possible that in the sulphur molecule, S_8 , a larger or smaller number of the sulphur atoms may be replaced by selenium. Rathke also considers that the characteristic decayed horseradish odor, when selenium is heated on charcoal, is due to carbon selenide, which, even in the most extreme dilution, has the same odor.

In his *Habilitationsschrift* (Breslau, 1903), Meyer shows that P_4Se_3 and P_2Se_3 are to be looked upon as distinct chemical compounds, but that P_4Se and P_2Se do not exist.

¹ This Journal, 24, 1070.

² Ber. d. chem. Ges., 36, 244.

³ Ibid., 38, 2207.

⁴ Ibid., 36, 418.

⁵ Ibid., 36, 2437.

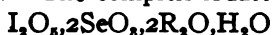
⁶ Compt. Rend., 136, 1551.

⁷ Proc. Chem. Soc., 18, 197.

⁸ Ztschr. anorg. Chem., 34, 187.

⁹ Ber. d. chem. Ges., 36, 594.

Several interesting classes of double salts or selenates with iodates, phosphates and arsenates have been prepared by Weinland and Barttlingck.¹ The complex iodates are of the formulas



and



the phosphates and arsenates follow the types



and



All these salts crystallize well.

Some considerable work has been done along the line of improvements in the electrolytic preparation of calcium. Borchers and Stockem² use fused calcium chloride as the electrolyte, starting the current through a thin carbon rod. Their calcium is spongy, but may be pretty thoroughly freed from calcium chloride by squeezing when fused. They prepare strontium by the same method, and find it is as soft as lead. Arndt³ modifies this method by using the electric arc, and obtains a calcium 99 per cent. pure. Ruff and Plato⁴ discuss the subject very fully, and describe their process for producing the metal, either on a small or on a large scale. The most important point in their process is the use of a mixture of calcium salts as an electrolyte. The best mixture they find to be about 1 part of fluor-spar to 6 of calcium chloride. Their calcium is pure white, somewhat harder than lead.

Goodwin and Smith⁵ describe an apparatus for the preparation of calcium by the electrolysis of calcium chloride.

The difficulties attending the electrolytic preparation of barium are shown by Guntz⁶ to be due to the formation of a 'basic' chloride, BaCl , which he has prepared in a pure state. This chloride forms double salts with the alkali chlorides, which are also formed when barium chloride is heated with metallic sodium or potassium.

Attention is called by Granger⁷ to the fact that at 600° aluminum becomes granular and exceedingly brittle. At a somewhat higher temperature it is very soft as well as granular, and is easily pulverized in small quantities. In the *Comptes Rendus* (135, 791), Verneuil discusses, at some length, the conditions necessary for the production of artificial rubies. It appears, among other conditions, that the temperature must be but little above the point of fusion of alumina, else the melted mass will

¹ *Ber. d. chem. Ges.*, 36, 1397.

² *Ztschr. Elektrochem.*, 8, 757.

³ *Ibid.*, 8, 861.

⁴ *Ber. d. chem. Ges.*, 35, 3612.

⁵ This Journal, 28, 873.

⁶ *Compt. Rend.*, 136, 749; *Bull. Soc. Chim.* (3), 29, 490.

⁷ *Bull. Soc. Chim.* (3), 27, 789.

become opaque on cooling. In less than two hours, Verneuil prepared a ruby of nearly 3 grams weight, which could not be distinguished from the natural stone. The utmost accuracy in conforming to the necessary conditions is demanded to attain such a result.

During the past year a considerable amount of work has been done upon thallium. Especially has there been an effort to obtain thallium alums, in which thallium is the trivalent metal. Numbers of double sulphates have been obtained by Marshall,¹ and Meyer and Goldschmidt,² but in no case an alum. The nearest approach to a solution of the problem is by Piccini and Fortini,³ who have prepared mixed crystals of ammonium alum in which a portion of the aluminum is replaced by thallium. They have not succeeded, however, in preparing the pure thallium alum. The thallium oxalates have also interested Meyer and Goldschmidt,⁴ as well as Rabe and Steinmetz,⁵ particularly in the effort to form complex thallium salts. While their efforts in this direction were not attended with success, numerous new, double oxalates were discovered. Meyer and Goldschmidt also prepared double salts of thallic acetate and of thallic nitrate, both rather rare classes of salts.

Investigations upon the rare earths have not been neglected during the past year, though few new ideas have been brought out. Drossbach⁶ splits didymium into its components by the use of a concentrated potash solution, and the recrystallization of the double magnesium nitrate. From a potash solution containing cerium, lanthanum and didymium, he precipitates pure cerium quantitatively by a current of chlorine. Meyer and Koss⁷ have studied the iodimetry of cerium dioxide and the didymium oxides, perfecting a method for the estimation of the former. Following up his work upon the preparation of the anhydrous chlorides of neo- and praseodymium, Martignon⁸ has studied the effect of heat upon the chlorides of samarium, yttrium and ytterbium in a current of dry hydrogen chloride. $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ loses 5 molecules of water at 110° and the last at 150° . Anhydrous samarium chloride is a yellow powder darkening with heat and fusing to a dark brown liquid at about 1000° , but regaining its original color on cooling. It is very deliquescent and evolves much heat on solution in water. The anhydrous chlorides of yttrium and ytterbium are very similar to that of samarium.

¹ *Proc. Roy. Soc. (Edin.)* 24, iii, 305.

² *Ber. d. chem. Ges.*, 36, 238.

³ *Ztschr. anorg. Chem.*, 31, 451.

⁴ *Loc. cit.*

⁵ *Ber. d. chem. Ges.*, 38, 4447.

⁶ *Ibid.*, 38, 2826.

⁷ *Ibid.*, 38, 3740.

⁸ *Compt. Rend.*, 134, 1308.

Starting with a mixture of the yellow oxides obtained in the preparation of didymium from monazite by the chromic acid method and fractioning with ammonia and then with oxalic acid, Marc,¹ while failing to isolate terbia, has thrown light upon the subject. He concludes that the so-called terbia is a mixture of yttria and another heavier earth, probably ytterbia, colored with a small amount of the real terbia. Terbium has two oxides, the lower white and the higher colored. It probably has an absorption spectrum in which the principal band is $\lambda = 464\text{--}461$. Its atomic weight should be about 157. Cleve's thulia he considers to be an yttria-ytterbia mixture with a little holmia and terbia, and Cleve's decipia a gadolina-yttria mixture colored with praseodymia. Cleve has separated out a very pure ytterbia and described a long list of its salts.² Ytterbium is always trivalent and resembles most closely yttrium and erbium. Rosenheim³ has described a large number of new thorium salts, some of them with organic acids. He also finds thorium chloride to form compounds with many organic oxygen compounds such as alcohol, aldehyde, acetone, and benzaldehyde.

According to Elba, by the electrolysis of hydrochloric acid with a lead anode PbCl_2 is formed, but with two anodes, one of lead and one of carbon, the PbCl_2 formed is oxidized by the chlorine at the carbon anode to PbCl_4 . The double chloroplumbates can be prepared in this way, and the slightly soluble quinoline salt can be used to determine the production of the tetrachloride quantitatively.⁴ Seyewetz and Trawitz⁵ prepare the ammonium chloroplumbate by adding a moist lead dioxide in small portions to an excess of concentrated hydrochloric acid at 0° , and also⁶ by the action of ammonium persulphate on lead dichloride. The chloroplumbate is used by them as a very effective agent for chlorination in organic chemistry.

Titanium trichloride and other compounds of trivalent titanium have been found by Knecht⁷ to be excellent reducing agents, far more powerful than stannous chloride. Among other instances, nitro compounds are instantly reduced to amines.

By electrolytic reduction Piccini and Marino⁸ have prepared a number of salts of bivalent vanadium. The sulphates belong to the ferrous-iron type, crystallizing alone with 7 molecules of water, and as alkali double salts with 6 molecules. Isomorphous, crystal mixtures were formed of vanadium-magnesium, and of vanadium-ferrous sulphates. Quadrivalent vanadium is being

¹ *Ber. d. chem. Ges.*, 35, 2382.

² *Ztschr. anorg. Chem.*, 32, 129.

³ *Ibid.*, 35, 424.

⁴ *Ztschr. Elektrochem.*, 8, 512.

⁵ *Bull. Soc. Chim.* (3), 29, 455.

⁶ *Compt. Rend.*, 126, 686.

⁷ *Ber. d. chem. Ges.*, 36, 166.

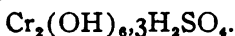
⁸ *Ztschr. anorg. Chem.*, 32, 55.

investigated by Koppel and Behrendt.¹ In their first communication they described a series of simple and double vanadyl sulphates, and another of sulphites.

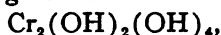
An extended investigation of chromium salts has been begun by Wyruboff,² with especial reference to the constitution of the violet and green modifications. He considers that the violet salts always contain the group $\text{Cr}_2(\text{OH})_6$, to which the acid is added. Thus the hydrated violet sulphate has the formula



while the anhydrous form is



On the other hand, the green salts contain the radical



in which two hydroxyls are acid and four basic. Thus we have the green salts



and



The formation from the violet salt is not merely a loss of water, but often a loss of acid. The chromosulphuric acids exist in several modifications, the first member of the series having the formula



the last two hydroxyls being acid in their nature. Wyruboff holds that many of the seemingly simple inorganic compounds are in reality very complex and must be likened in their constitution to the compounds of organic chemistry. By the action of hot concentrated hydrochloric acid, Recoura³ finds that chromium sulphate is converted into a chlorosulphate,



in which the chlorine is not immediately precipitable by silver nitrate, while the sulphate group is immediately precipitated by barium chloride. On heating this compound to 85° , it gradually loses 1 molecule of water, the sulphate group is no longer affected by the barium chloride, and its aqueous solution is a non-electrolyte. Aluminum forms a similar chlorosulphate, but iron does not.

The question of the existence of bichromates of any metals except those of the alkalis has been settled by Autenrieth,⁴ who prepares silver bichromate, $\text{Ag}_2\text{Cr}_2\text{O}_7$, by double decomposition in the presence of nitric acid, and also by the action of silver nitrate on chromium trioxide. Barium bichromate was also obtained, but not lead bichromate. He further clears up the reac-

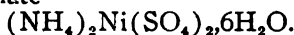
¹ *Ztschr. anorg. Chem.*, **38**, 154.

² *Bull. Soc. Chim.* (3), **27**, 666, 719.

³ *Compt. Rend.*, **138**, 163.

⁴ *Ber. d. chem. Ges.*, **38**, 2057.

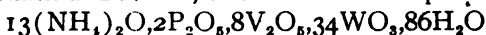
tion, for the preparation of chromyl chloride, by finding that while a 20 per cent. hydrochloric acid gives, with chromium trioxide, only chlorine, if the acid is 35 per cent. to 40 per cent. strong, a large amount of the chromyl chloride is obtained. A double chromate has been at last prepared by Briggs,¹ who, by the action of ammonium chromate on nickel sulphate, has obtained the ammonium nickel sulphate



The pure potassium salt was not made, but an isomorphous mixture of the potassium-nickel sulphate and chromate was obtained.

Doering² has made an extended study of a chromium, 97 per cent. to 98 per cent. pure, prepared by the Goldschmidt process. The metal is rapidly dissolved by hydrochloric acid, CrCl_2 being first formed, but the whole being eventually converted into CrCl_3 . Since in a hydrogen atmosphere the bichloride is rapidly converted into the trichloride only in the presence of catalytic agents, such must be present in this solution of chromium. This agent was found to be Geuther's oxide of silicon, $\text{Si}_3\text{H}_2\text{O}_8$, formed from the silicon present as an impurity in the chromium. The fusing-point of a similar chromium, 99 per cent. pure, was found by Lewis³ to be 1515° .

Several pieces of valuable work on tungstates have been carried out in the laboratory of the University of Pennsylvania under the direction of Dr. Edgar F. Smith, and published in this Journal.⁴ The so-called para- and metatungstates have been investigated by Taylor, who finds all the known ammonium salts to have a complex formula. He assumes that in all these salts the group $2\text{NH}_4\text{OH} \cdot 4\text{WO}_3$ is present as a nucleus, the side chains containing varying proportions of $\text{NH}_4\text{OH} \cdot \text{WO}_3$ and H_2O . A new class of complex tungstates, containing vanadium and phosphorus, or arsenic, in different stages of oxidation, has been described by Smith and Exner, and further developed by Rogers.



may be cited as an example of one of these salts. Friedheim and Henderson⁵ have described a somewhat similar class of tungstates containing vanadic and silicic acids.

Interest in the subject of colloids has greatly increased among chemists since Bredig's work upon colloidal platinum and several new methods of preparing metallic and other colloids have been recently described. By means of hydrazine hydrate, hydroxylamine hydrochloride, or hypophosphorous acid, Gutbier⁶ obtains hydrosols of gold, silver, platinum, mercury, and copper, as well

¹ *J. Chem. Soc.*, 83, 401.

² *J. prakt. Chem.* (2), 66, 65.

³ *Chem. News*, 86, 13.

⁴ This Journal, 24, 573, 629; 25, 298.

⁵ *Ber. d. chem. Ges.*, 35, 3242.

⁶ *Ztschr. anorg. Chem.*, 31, 448; 32, 292, 347.

as of selenium and tellurium. The gold hydrosol prepared by the action of hydrazine on a dilute neutral solution of gold chloride, is blue and resembles that obtained by Bredig electrolytically. It is very stable in the cold, but on warming is immediately converted into the hydrogel. Gutbier also obtains hydrosols of tellurium disulphide and trisulphide, and of selenium disulphide. Kuespert uses formaldehyde as his reducing agent¹ in the presence of water-glass. He prepares a hydrosol of copper acetylide by adding a trace of copper and ammonia to water, which has been shaken up with acetylene. Henrich's reducing agents² are the photographic developers, of which he finds pyrogallol the best for the production of colloidal metals. By varying his solvents, he gets organosols of gold with ether, acetone, and alcohol. He calls attention to the fact that in the electric current the metal of a hydrosol moves toward the positive pole. While the method of Bredig failed to give colloidal mercury, this has been prepared electrolytically by Billitzer³ by the electrolysis of a very dilute solution of mercurous nitrate with a current of 220 volts at 0.2 to 0.3 amperes. An interesting colloid of silver (and mercury) oxide, under the name of collargol, is prepared by Paal⁴ by adding caustic soda to a solution of silver nitrate and sodium protalbinat, or lysalbinat. On warming the solution, colloidal silver is formed, and colloidal gold may be prepared in a similar way. Within the past few months there has been some little discussion as to whether or not the silver in collargol is in chemical combination. The colloidal hydroxides have been studied by Biltz,⁵ who prepares them by the dialysis through parchment paper of a dilute solution of the nitrates, the reaction being hydrolytic. Nitrates are chosen from the fact of their lesser influence in promoting the formation of a hydrogel, since some of the acid remains present after dialysis, in the form of a basic nitrate. By a similar method, Melikoff⁶ obtains from potassium percolumbate, colloidal percolumbic acid, from which oxygen is evolved on standing, or more rapidly by the addition of concentrated sulphuric acid. This indicates that percolumbic acid is not to be looked upon as a compound of hydrogen peroxide.

But little work has been done upon the inert gases of the atmosphere. By working on a large mass of air (191.1 kg.), Ramsay⁷ has studied more completely krypton and xenon, the boiling-points of which are respectively -151.7° and -109.1° . The amount of krypton in the atmosphere is estimated as 1 volume in 20,000,000, and that of xenon as 1 volume in

¹ *Ztschr. anorg. Chem.*, 34, 453; *Ber. d. chem. Ges.*, 38, 2815, 4066.

² *Ber. d. chem. Ges.*, 36, 609.

³ *Ibid.*, 38, 1929.

⁴ *Ibid.*, 38, 2206, 2219, 2224.

⁵ *Ibid.*, 38, 4431.

⁶ *J. Russ. Phys.-Chem. Soc.*, 38, 457.

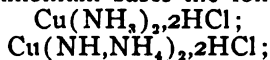
⁷ *Chem. News*, 87, 159.

170,000,000. By a comparison of the spectra, Liveing¹ concludes that the presence of the inert gases in the sun is exceedingly probable. The spectra of these gases have been more thoroughly studied by Baly,² and from the spectra of krypton and xenon it seems probable that some unknown element of higher atomic weight is present.

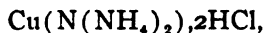
That subject which has attracted more attention than any other during the past year has, undoubtedly, been radio-activity. Even a brief outline of the work done would require much space, and there may be a question as to how far this subject belongs to chemistry. Two points of interest may, however, be noted. It was recently currently reported that Huggins had found the spectrum of radium to be, in part, identical with that of helium, but this has since proved to be a mistake. It appears, however, that Ramsay has actually obtained helium in the emanations from radium. It also seems, from the most recent reports, that Curie finds the energy of radium to be given off more actively at extremely low temperatures than at higher.

Some little has been done upon the metal-ammonias and metal-ammonium bases. Barium-ammonia has been carefully investigated by Guntz and Mentrel.³ At temperatures not above 28°, barium unites directly with ammonia, forming the compound $\text{Ba}(\text{NH}_3)_6$. Below -23° this compound is stable, but above that begins to decompose, forming barium amide, $\text{Ba}(\text{NH}_2)_2$, which is also formed by the action of ammonia on barium at 280°. At 650° the amide is decomposed into barium nitride, Ba_3N_2 . The action is reversible, and below 680° barium nitride unites with ammonium to form the amide. It is worthy of note that by the action of carbon monoxide upon barium-ammonia, barium carbonyl, $\text{Ba}(\text{CO})_2$, is formed, a yellow body, fairly stable, but decomposing in the air or moisture. Sodium and lithium form compounds much similar to those of barium. The cesium and rubidium-ammonia have been prepared by Moissan,⁴ and have the formula CsNH_3 and RbNH_3 .

The copper-ammonium bases have been the subject of continued investigation by Bouzat.⁵ He suggests for the constitution of the three cupri-ammonium bases the following:



and



formulae which seem rather a step backward toward the old Blomstrand theory. Several of the metal-ammonium bases have been studied from the standpoint of physical chemistry by Euler⁶

¹ *Proc. Cambr. Phil. Soc.*, 12, 11, 87.

² *Proc. Roy. Soc.*, 72, 64.

³ *Bull. Soc. Chim.* (3) 29, 585.

⁴ *Compt. Rend.*, 136, 1177.

⁵ *Ann. chim. phys.* (7), 26, 479; 29, 305.

⁶ *Ber. d. chem. Ges.*, 36, 1854.

and Bonsdorff.¹ The complex cations are all strong bases, $\text{Ag}(\text{NH}_3)_2$ being comparable with the alkalis, its hydroxide being more strongly dissociated than barium hydroxide. The cadmium cation is $\text{Cd}(\text{NH}_3)_4$, and that of zinc $\text{Zn}(\text{NH}_3)_4$. In this connection it may be noted that Bonsdorff obtained argento-cyanic acid, $\text{HAg}(\text{CN})_2$, by solution of silver cyanide in HCN and it proves to be a very strongly dissociated acid. Apropos of the Werner hypothesis, Kremann² has described an interesting experiment in which the colored complex ions of the luteo-, purpureo- and praseo-cobalt bases migrate to the cathode, while the colored ions of potassium diamino-cobaltonitrite migrate to the anode, as is demanded by the theory. Werner and Goslings³ discuss the carbonato-cobalt amines, showing that the CO_2 group can enter the co-ordinated nucleus of a molecule, occupying a single co-ordinated position. They, however, seem to assume that it is linked by one unit of combining power to one of the ammonium groups. Several new carbonato-pentamine salts are described by them.

There appears to be a renewed interest of late in those fields which lie in both inorganic and organic chemistry, the organic compounds of inorganic elements. Wyruboff⁴ has examined the didymium and double glucinum oxalates; Guerbet,⁵ the lactates of mercury; Buroni,⁶ the mercurous and halo-mercurous salicylates; Biilmann,⁷ the mercury salts of many other organic acids; Howe and Smiley,⁸ chrom-malonic acid and some of its salts; Pictet,⁹ acetyl-nitric and acetyl-chromic acids, as well as¹⁰ boroacetates, boro-butyric acid, etc.; and Pope and Peachy,¹¹ halo-derivatives of stanni-methane.

In conclusion may be noticed a paper read by Dewar before the Royal Society,¹² giving the density and the coefficient of expansion of ice, carbon dioxide, hydrated salts, and many other compounds, at low temperatures, generally at about -188° . The interesting point is brought out that the density of ice never becomes as great as the least density of liquid water, or, as expressed by Dewar, the ice molecules can never approach so near each other by thermic contraction as are the molecules of liquid water.

¹ *Ber. d. chem. Ges.*, 36, 2322.

² *Ztschr. anorg. Chem.*, 33, 87.

³ *Ber. d. chem. Ges.*, 36, 2378.

⁴ *Bull. Soc. Franc. Min.*, 28, 66, 71.

⁵ *J. Pharm. Chim.* (6), 16, 5.

⁶ *Gazz. chim. ital.*, 32, 11, 305.

⁷ *Ber. d. chem. Ges.*, 38, 2571.

⁸ *This Journal*, 28, 444.

⁹ *Arch. Sci. Geneve*, 18, 589; *Ber. d. chem. Ges.*, 38, 2526; 36, 2215.

¹⁰ *Ber. d. chem. Ges.*, 36, 2219.

¹¹ *Proc. Roy. Soc.*, 72, 7.

¹² *Chem. News*, 88, 277, 289.

NOTE.

Further Facts Regarding "Ureine."—The September number of the Journal (Review of American Chemical Research, p. 396) gives an abstract of the latest repetition of the "ureine" fallacy, this time published in *Le Physiologiste Russe*.

About three years ago, Dr. William Ovid Moor began his series of communications on "The Discovery of Ureine, the Principal Organic Constituent of Urine and the True Cause of Uraemia."¹ The announcement of the alleged discovery was made in such extravagant terms that it was next to impossible to have any faith in the results and conclusions Dr. Moor brought forward. Thus, "ureine" was said to be the "most characteristic component part of urine," existing in "a quantity superior to urea." "Ureine belongs to the group of alcohols of the aromatic series," wrote Dr. Moor; in another part of the paper it was referred to as "a ferment" with "a potential energy of at least 130° C.," "being the principal cause of the ammoniacal fermentation of urine, as without its presence urea cannot be decomposed into ammonia and carbon dioxide." "Without ureine," it was further stated, "all organic matter would become converted into urea, which would remain in nature without any use, and thus, within a limited period of time, all vegetation and animal as well as human life would cease."

Shortly after Moor's first publication, Chace and I failed completely to obtain any of Moor's essential results, in spite of special care in all our operations. We were able to show, however, that "ureine" is a *mixture* of substances—in fact, merely urine, *minus* most of its water and urea, and some of the other constituents, *plus* material added to and formed in it during the manipulations. Employing customary methods of separation and detection, *purified* "ureine" has been found to contain sodium, potassium, ammonia, phosphate, urea, creatinin, pyrocatechin, phenol-alkaloidal substances and purin bases. Other urinary substances are present, which we have not attempted to identify. Although we avoided excess of mercuric nitrate in the process of decolorization, following Moor's method precisely, we always found mer-

¹ Moor: "The Discovery of Ureine, the Principal Organic Constituent of Urine and the True Cause of Uraemia." Communication presented to the Thirteenth International Medical Congress, Paris, 1900. Published in the *Medical Record*, 88, 326 (September 1, 1900).

cury in "ureine." Doubtless a soluble compound of mercury was formed in the "purification" process. Nitrate and oxalate, also introduced during this so-called purification, were constant constituents. Shaken repeatedly with excess of ether in a separatory funnel, "ureine" gradually separates into several layers of different color and degrees of transparency, and the ether itself takes on a yellowish tinge. Samples that had been allowed to stand exposed to the air for several months deposited crystals of urea. The amount of ash from four preparations varied from 9 to 24 per cent. A wax-like mass can be obtained immediately on treatment of the "ureine" with concentrated nitric acid. When this mass is broken up mechanically in an excess of nitric acid and examined under the microscope, crystals of urea nitrate are seen to cover the field.

Our general conclusions¹ have been that "ureine" is a *mixture*, containing several of the organic substances, and a considerable proportion of inorganic matter, ordinarily found in normal urine; also matter introduced with reagents in the so-called purification process. Further, the toxicity of "ureine" is due to some of the normal urinary constituents, such as the potassium and the alkaloidal bodies, and to the radicals introduced in "purifying." Consequently, much as it is to be regretted, "ureine" does not furnish a clue to the cause of uraemia nor can any of Dr. Moor's biological deductions regarding "ureine" be accepted.

Our criticism of Moor's work and conclusions in this connection have been endorsed by several investigators, but none of the questions raised by us has ever been answered by Dr. Moor. In the meantime, however, "ureine" is being exploited in the same manner in one journal after another, and impossible chemistry and biology receive wide circulation.

WILLIAM J. GIES.

LABORATORY OF PHYSIOLOGICAL CHEMISTRY
OF COLUMBIA UNIVERSITY.

NEW BOOKS.

THE ELEMENTS OF ELECTRO-CHEMISTRY, TREATED EXPERIMENTALLY.
By DR. ROBERT LÜPKE. Second English edition, translated from the fourth German edition. By M. M. PATTISON MUIR. 250 pp. Price, \$2.50. Philadelphia: J. B. Lippincott Company.

The work is divided into three parts: (1) Recent theories of

¹ Chace and Gies: "Some Facts Regarding 'Ureine,'" *Medical Record*, 89, 329 (March 2, 1901); also Gies and collaborators: "Biochemical Researches," reprint No. 31 (1903).

electrolysis, 79 pages; (2) the theory of solutions of van't Hoff, 44 pages; (3) the osmotic theory of the current of galvanic cells, 119 pages. Under these headings, Dr. Lüpke has presented, in very readable and easily comprehended language, the present status of the subject. The experimental part is easily the best part of the book, the experiments being very well chosen and very suitable for bringing out the principal facts of the science. If the teacher using the work will confine his pupil's attention to the experiments and the facts which they teach, both teacher and student will be very much helped by the book. If, however, the student wanders into the theoretical part of the book, he will learn, along with much which is good, also much which is questionable, and he will need close attention from his teacher to keep him from receiving distorted ideas. The weak side of the theoretical part is that it presents many of the generalizations of the dissociation theory as if they were without exceptions, and ignores many recent proofs of the failure of the theory in some special cases. Part of Faraday's generalizations are credited to von Helmholtz, simply because, apparently, the latter discussed them in a lecture, while Le Blanc is credited with the discovery of a law regarding the voltage necessary to decompose a compound, which is merely a re-statement of Thomsen's rule, coupled with Hess's law of thermo-neutrality. These, perhaps unconscious, appropriations of electrochemical honors for German scientists will perhaps make the book more popular in Germany, but decrease its reliability for general use.

The translator and publishers have done their work very well.

JOSEPH W. RICHARDS.

ARBEITSMETHODEN FÜR ORGANISCH-CHEMISCHE LABORATORIEN: EIN HANDBUCH FÜR CHEMIKER, MEDIZINER UND PHARMAZEUTEN. VON PROFESSOR DR. LASSAR-COHN. Dritte, vollständig umgearbeitete und vermehrte Auflage. Hamburg und Leipzig: Leopold Voss. 1901-1903. xvi + 1241 pp. Price, 38 marks.

The second edition of this work is well known, both in the original and in the excellent translation of Alexander Smith. The material included in the present edition is more than twice as great as that of the second. The work consists, first, of a "General Part," (213 pages) which discusses general operations such as extraction with ether, distillation, dialysis, sealed tubes, decolorizing of liquids, filtration, crystallization, solvents, determina-

tion of molecular weights, melting-points and boiling-points, sublimation and drying. Methods used in the determination of other physical properties, such as specific gravity, viscosity, heat of combustion, refractive index, specific rotation and electrical conductivity are not mentioned.

The "Special Part" is devoted to a discussion of the more important processes used in the preparation and study of organic compounds, and includes the following topics: Formation of acyl and benzenyl derivatives, and of oximes and hydrazones; fusion with alkalis; introduction of halogens; replacement of halogens; preparation of salts and alkaloids; preparation of diazo compounds; esterification of acids and etherification of phenols; condensation; formation of nitro compounds; separation of isomers; saponification of cyanides and esters. The book concludes with a description of the methods for the ultimate analysis of organic compounds.

As the author of the work points out, the literature of this subject has grown to such overwhelming proportions that it is often extremely difficult to find the method best suited for a particular purpose. The general indexes are usually of little service, since methods of working are, in general, described as incidental to the preparation of some compound, and only the name of the latter is to be found in the index. Professor Lassar-Cohn's book serves a most useful purpose in this direction. The various topics are illustrated by thousands of examples taken from the literature. In the present edition many of these have been taken from the patents, and when we consider the rigid commercial requirement that a method must, if possible, give a good yield, it is easily seen that workers in scientific laboratories may secure very many valuable suggestions from this source.

The experience of the author would seem to have been almost exclusively with aromatic compounds. For this reason the work is somewhat deficient in methods which are especially adapted to aliphatic bodies. English and American journals seem to have been almost completely ignored in the preparation of the book, and in a number of places the author's knowledge is incomplete or one-sided for this reason.

It is very unfortunate that the author has not furnished a general index, which should include all of the compounds men-

tioned in the book. Even the special indexes, at the close of each section, are not so complete as they should be.

In spite of these faults, the book is a very valuable one, and it should be in every laboratory where work in organic chemistry is done.

W. A. NOYES.

QUANTITATIVE ANALYSIS, ADAPTED FOR USE IN THE LABORATORIES OF COLLEGES AND SCHOOLS. BY FRANK CLOWES, D.Sc., AND J. BERTRAND BERNARD COLEMAN, A.R.C.Sc. Philadelphia: P. Blakiston's Son & Co. 1903. Sixth edition. 602 pp., 125 cuts. Price, \$3.50.

This is the sixth edition of a work which, in some one or more of its previous editions, is to be found in most chemical libraries. The main changes are a revision of the section on organic analysis and the addition of methods for the determination of aluminum and nickel in steel, the analysis of aluminum alloys and a table of four-place logarithms. The Gooch crucible is described for the first time, but only in the appendix, and its use is nowhere recommended in the text. The work is still distinctively English and does not always accord with American ideas, or the best and latest practice. This is especially noteworthy in the sections on superphosphates, milk, nitrogen and silicates. The methods given are clearly described and the cross-references are so full and complete that even the routine analyst could scarcely fall into errors of procedure. Little attempt is made, however, to view quantitative analysis from the scientific standpoint.

The book covers a much larger field of analysis than would seem possible from its size. This is due to the fact that there is almost no repetition, and is made possible by the excellent system of cross references already mentioned. The opening descriptive chapters on chemical manipulation are unusually clear and concise. These are followed by numerous, simple gravimetric and volumetric determinations, to be themselves succeeded by a long list of general quantitative analyses covering a wide field.

The book will be found useful in all laboratories and will be serviceable to students under proper guidance. It is well printed and has a good index.

C. L. PARSONS.

THE SUGAR-CANE IN EGYPT. BY WALTER TIEMANN, Member of the Society of German Sugar Technicians and of the Association des Chimistes de Sucreries et Distilleries, Paris. x + 74 pp. Price, 5/- net.

This work, by the director of the experimental station in Upper Egypt, treats of the sugar-cane industry only from the agricul-

tural standpoint and in such a manner as to excite nothing but admiration for the scientific exactness with which the experiments in intensive culture were prosecuted. It is shown that modern methods must supplant the Arabs' indifference to the basic rules of rational cultivation.

The author discusses depletion of soil by a defective tenant system, best native cane varieties, details of cane selection, planting, cultivation and harvest, proper conditions of the seasons and prevailing meteorological conditions. The five years of experimental work were controlled by digestion analyses of the canes, systematically tabulated. Alluvial, coal and limestone deposits are described and their analyses given. We find excellent, practical information regarding native manures, such as stable dung, "ruins manures," zebach balladi, dove guano, bat guano and their accumulation, with analyses. The author states a need for imported artificial fertilizers and green manures, and adds practical formulae of tried fertilizer combinations, with cost and returns.

The instructions for carrying out the system for a manurial experiment, as adopted by Dr. Weitz, secretary to the Delegation of the United Association of Saltpeter Manufacturers in Berlin, embody some most practical suggestions, if accurate deductions are to be made.

Chapters VII and VIII, 27 pages, present the manurial experiments in detail, comprising acreage, character of cane produced, fertilizer applied, crop yield and cane analyses; *i. e.*, sp. gr., Beaumé, Brix, juice per cent., non-sugar, quotient, sucrose, glucose and weight.

The material is well arranged, amply illustrated and fully supplemented by plotted tables. The style is very lucid and the presentation is shorn of unnecessary detail. D. L. DAVOLL, JR.

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